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Lithium-ion Battery Safety Issues for Electric and Plug-in Hybrid Vehicles

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16. Abstract This report summarizes an assessment of potential lithium-ion (Li-ion) battery vehicle safety issues to provide NHTSA information it can use to assess needs and prioritize its future research activities on Li-ion battery vehicles. This analysis is intended to assist NHTSA in identifying potential critical operational safety issues it may want to consider and in assessing if further testing is needed to evaluate safety concerns. This document is the comprehensive final report for the project, compiling and summarizing the key background information and assessment of results developed. The scope of this investigation includes plug-in hybrid electric vehicles, hybrid-electric vehicles, and battery electric vehicles. This report reviews the literature for cell chemical and mechanical design and safety, battery architecture and design, vehicle systems relative to battery power, battery management and control systems, safety standards, and a survey of experimental, concept, prototype, and production-scale vehicles that employ Li-ion battery systems for propulsion.			
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List of Abbreviations

Abbreviation	Meaning
AC	alternating current
AEI	Automotive Engineering International (magazine)
BEV	battery electric vehicle
BMS	battery management system
CAN	controller area network
C-E	collector-emitter
CID	current interrupt device
CO	carbon monoxide
CV	cyclic voltammagram
DC	direct current
DEC	diethyl carbonate
DMC	dimethyl carbonate
DSP	digital signal processor
DUT	device under test
EC	ethylene carbonate
EESA	electrical energy storage assembly
EMI	electromagnetic interference
ECU	electronic [or engine] control unit
ESD	electrostatic discharge
EV	electric vehicle
FET	field effect transistor
FMEA	failure modes and effects analysis
FMECA	failure modes and effects criticality analysis
FMVSS	Federal Motor Vehicle Safety Standards
HEV	hybrid electric vehicle
HF	hydrofluoric (acid)
IC	internal combustion
ICE	internal combustion engine
IDIQ	indefinite delivery/indefinite quantity
IEC	International Electrotechnical Commission
IEEE	The Institute of Electrical and Electronics Engineers, Inc.
ISO	International Organization for Standardization
LCO	lithium cobalt
LFP	lithium iron phosphate
LiF	lithium fluoride

Abbreviation	Meaning
Li-ion	lithium-ion
LMO	lithium manganese (or manganate)
LTO	lithium titanate
MEMS	micro-electromechanical system
MSDS	Material Safety Data Sheet
NCA	nickel cobalt aluminum
NCM, NMC	nickel cobalt manganese
NHTSA	National Highway Traffic Safety Administration
NiCAD	nickel-cadmium
NiMH	nickel metal-hydride
NREL	National Renewable Energy Laboratory
OEM	original equipment manufacturer
PAM	parallel array of modules
PASC	parallel array of series cells
PC	propylene carbonate
PCM	protection circuit module
PE	polyethylene
PHEV	plug-in hybrid electric vehicle
PP	polypropylene
PTC	positive temperature coefficient
PVDF	polyvinylidene fluoride (also poly vinylidene difluoride)
PVdF-HFP	poly(vinylidene fluoride)-hexafluoropropylene
Rdc	internal direct current resistance
RESS	rechargeable energy storage system
SAE	SAE International
SEI	solid-electrolyte interface (also solid- <i>electrode</i> interface)
SEM	scanning electron microscope
SLI	starter-lighter-ignition
SOC	state of charge (0 to 100%)
SOH	state of health
TCO	temperature cutoff
UL	Underwriters Laboratories
U.N.	United Nations
UNECE	United Nations Economic Commission for Europe
VCE	collector-emitter voltage
VRLA	valve-regulated lead-acid

Executive Summary

Report Overview

The objective of this Task Order was to assess potential Li-ion battery vehicle safety issues and provide NHTSA information it can use to assess needs and prioritize its future research activities on Li-ion battery vehicles. This analysis is intended to assist NHTSA in identifying potential critical operational safety issues it may want to consider and in assessing if further testing is needed to evaluate safety concerns. This document is the comprehensive final report for the project, compiling and summarizing, in a single document, the key background information and assessment results developed during the course of this investigation. This document is intended to provide a compendium of available technical background information relevant to the safety of Li-ion battery systems for vehicles to inform NHTSA and to support its assessment of research and development needs.

This report is organized into the following chapters and appendix.

- Chapter 1. Introduction
- Chapter 2. Li-ion Cell Electrochemistry and Safety Performance
- Chapter 3. Li-ion Cell Design and Safety Performance
- Chapter 4. Li-ion Battery System Architecture
- Chapter 5. HEV, PHEV, and BEV Battery System Analysis
- Chapter 6. Battery Management and Control Systems
- Chapter 7. Battery Conditions that Enhance the Initiation and Growth of Internal Shorts
- Chapter 8. Overview of Relevant Safety Standards
- Chapter 9. Codes and Standards Comparison and Gap Assessment
- Chapter 10. Potential Hazards, Risks, and Risk Mitigation Strategies
- Chapter 11. Summary of Observations and Considerations
- Appendix. Survey of Li-ion Battery Vehicles

Chapter 1 serves as an introduction to the report. Chapter 2 discusses Li-ion battery electrochemistries currently available or being developed for electric vehicles, candidate component materials and their electrochemical interactions, and electrochemical performance, hazards and failure modes of different cell chemistries. Chapter 3 describes the design and construction of Li-ion battery cells, focusing on their electrical, thermal, mechanical, and safety characteristics. Chapter 4 describes a potential generic design architecture and integration of Li-ion battery from the cell into a module, and joining modules to form a complete battery pack. Chapter 5 provides an overview of battery systems as used in various vehicle power configurations. Chapter 6 describes battery management systems that control charge and discharge and ensure safety during normal and abnormal operations. Chapter 7 focuses on the role of side reactions that can lead to an internal short circuit (internal short) and the influence of the operating conditions on the initiation and growth of this failure mode. The initiation of an internal short can be the first step in a cascade that leads to thermal runaway and other safety and performance events. Chapter 8 summarizes the current published safety guidelines and requirements from key Society of Automotive Engineers (standards for Li-ion battery vehicles. Industry standards have been developed to provide guidelines and qualification test requirements to help ensure the safety of Li-ion batteries for vehicles. Even as these standards have been published, industry has initiated development of enhanced versions because of the rapidly

evolving developments in Li-ion battery technology. Chapter 9 assesses potential gaps in design, manufacturing, and test standards intended to prevent or mitigate potential failure modes identified. A high-level approach was taken in this gap analysis, in which Li-ion battery standards were compared to standards for hydrogen vehicle fuel systems as a benchmark of a mature set of industry standards. It represents automotive industry consensus on minimum design and test requirements to achieve the desired level of safety for onboard vehicle energy storage systems. Chapter 10 integrates the results of the preceding chapters of the report to summarize potential hazards, risks, and risk mitigation strategies for Li-ion battery vehicle safety identified in the program. Chapter 11 provides a closing summary of observations and considerations.

The Appendix identifies vehicles that are available or under development as of Spring 2011, which use Li-ion batteries. This information includes vehicle specifications, vehicle performance specifications, motor drivetrain characteristics, and vehicle battery specifications.

Summary of Observations and Considerations

Lithium-ion battery systems show great promise for automotive and other vehicular applications, and are already being used successfully in a wide range of vehicle platforms. In terms of vehicle review and inventory, the report lists more than 40 vehicle models using Li-ion battery systems for propulsion, in experimental, concept, prototype, or full production cars, as of Spring 2011. These vehicles tend to be either compact, urban-scale cars built for extremely high efficiency, or advanced performance-type cars intended to replicate conventional internal combustionsports or racing cars. The cars use between 22 and 8,000 Li-ion cells for propulsion, with battery-only operating ranges from 100 miles up to 300 miles. Most of the vehicles evaluated have a top speed of 80 to 130 mph.

Automotive designers, manufacturers, and component suppliers are actively working to advance and improve the safety of Li-ion battery technology. The main failure concerns for these systems are heat dissipation, thermal runaway events, low-temperature charging conditions, crash/shock consequences, and the effects of cell stress and aging in the vehicle environment. Many fail-safe systems such as current limiting devices for charge and discharge management have been developed. The report presents idealized conceptual models of Li-ion battery modules and battery packs, showing the safety and battery management/control features and functions now available or in development.

Li-ion battery technology is in the development stage and is not yet settled. Substantial research and development is in progress to achieve greater Li-ion battery performance at lighter weight and lower cost. Researchers are exploring higher performance chemistries and are expanding the operating range of batteries through electrochemical modeling. As battery technology matures, the safety risks may increase as manufacturers attempt to obtain greater performance from existing chemistries and adopt new chemistries with less field experience. Increasing the bounds of performance implies operating the battery cells closer to limits where damage initiation and growth, leading to failure, can occur. While all manufacturers intend to deliver safe products, some may be more thorough than others, due to experience and/or resource availability. However, this does not suggest that organizational size and resource availability correlate directly to product safety.

Regarding the risk of electrochemical failure, the report concludes that the propensity and severity of fires and explosions from the accidental ignition of flammable electrolytic solvents used in Li-ion battery systems are anticipated to be somewhat comparable to or perhaps slightly less than those for gasoline or diesel vehicular fuels. The overall consequences for Li-ion batteries are expected to be less because of the much smaller amounts of flammable solvent released and burning in a catastrophic failure situation.

Another safety concern is the isolation of high-voltage components to protect passengers and first responders in the event of a crash. The loss of high-voltage isolation can manifest two hazards including short circuit of the battery causing a thermal event or high-voltage potential exposure to humans.

Li-ion electrochemistry failure processes are not self-limiting and require passive and/or active controls for management and safety. Li-ion failure processes may be understood as electrochemical or stress induced “damage” at the cell level that incubates, initiates, and grows until failure. Li-ion failure processes are time-dependent process. While failure can sometimes occur very rapidly after a cell is damaged, damage may also sometimes grow over many years and many duty cycles, causing delayed failure long after damage is initiated. Key parameters relevant to detecting and controlling damage growth are not currently measured, but are inferred through simplistic or sophisticated models.

The investigation conducted here demonstrates that there are numerous external events or processes in the life a vehicle that could contribute to damage and failure of a Li-ion battery. Damage and failure are broad terms used in this investigation to describe complex electrochemical processes resulting from electrical, thermal and mechanical stresses. In general, the technical literature indicates that, while there are many contributing factors, the primary parameters controlling Li-ion cell and battery performance are temperature and operating voltage. For each battery chemistry, design, and expected duty cycle, there is a range of temperatures and range of operating voltage in which electrochemistry is dominated by intercalation mechanisms. Outside this range, undesirable side reactions may occur which can lead to self-heating (exothermic reactions) and/or internal electrical shorts (excessive flow of electrons). Exothermic reactions and/or internal electrical shorts may be triggered by manufacturing defects, or mechanical, electrical, or thermal errors, misuse or abuse. If allowed to continue, these reactions or shorts can create conditions for self-heating within the cell; which grow to become uncontrolled increases in temperature and pressure (thermal runaway); and potentially end in venting or catastrophic failure of the cell.

For the purpose of this investigation, safety related *failure* occurs when electrochemical reactions within a cell become uncontrolled and self-propagating, exceeding the ability of the battery management system (passive and active) to maintain control. *Damage* is defined as irreversible electrochemical reactions outside the design charge/discharge intercalation mechanisms as well as stress induced fractures and cracks such as those caused by diffusion of the lithium into and out of the anode. Abuse and normal service charge/discharge cycles may cause damage to grow in a controlled fashion, until it becomes self-propagating and exceeds the capabilities of the battery management system.

Li-ion batteries are complex systems built to manage and control the electrochemical reactions in Li-ion cells to safely and efficiently receive, store, and discharge electrical energy while

preventing or mitigating failure causes. The results of this investigation identified seven primary categories of external causes contributing to failure of Li-ion battery cells .

- External electrical causes such as external electrical short, overcharging, or overdischarging
- External thermal causes such as exposure to high temperatures or charging at cold temperatures
- External mechanical causes, which include excessive shock, impact, compression (crush), or penetration
- External chemical contamination including packaging penetration by corrosive and aggressive agents and contamination of internal components by water, saltwater, or corrosive agents
- Service-induced stress and aging causes such as excess cycling that lead to electrochemical component breakdown, fracture and crack growth
- Cumulative abuse and service causes in which combinations of electrical, mechanical, and thermal abuse (summarized above) and normal charge/discharge duty cycles cause damage to initiate and grow to the point of failure
- Errors in design, manufacturing, operation, and maintenance, which induce electrical, mechanical, and thermal abuse causes

The contribution of these events or processes toward failure depends upon their contribution to electrochemical processes within a battery cell or series of cells.

For the purposes of this investigation, a hazard is the result of a failure that could lead to safety issues or consequences for vehicle passengers, first responders, and the public and surrounding property. The term “hazardous failure” is used in this report to indicate one of the following hazards.

- Potential primary hazards associated thermal runaway induced heat and pressure
 - Venting of high-temperature electrolytic solvent vapors, either through pressure relief devices or holes in the casing
 - Combustion and flammability of ejected flammable electrolytic solvent vapors
 - Local atmospheric overpressure
 - Cell casing rupture and release of projectiles (If pressure relief devices are not present or if they fail)
- Potential secondary hazards that develop as a consequence of the primary hazards
 - Release of toxic and incompatible (corrosive) materials
 - Asphyxiation
 - Ignition and burning of adjacent flammable vehicle components or surfaces
 - High-voltage electrical shock hazards, due to melting or burning of electrical insulation and isolators

The heat and pressure resulting from thermal runaway, as well as combustion of solvent vapors and local overpressure may create conditions for self-heating within *adjacent* cells, particularly if they are damaged by the similar defects, errors, misuse or abuse that damaged the first cell. Consequently, the potential exists for propagation of thermal runaway throughout a series of

cells within an array and module. The severity and consequences of particularly hazard are clearly multiplied through propagation beyond a single cell.

A number of recognized safety standards are in place to govern the manufacture and use of Li-ion batteries, including those integrated into vehicles, and to document their safety under demanding environmental conditions representative of highway use. Li-ion battery standards were compared to industry standards for hydrogen vehicle fuel systems to benchmark them against a mature set of standards. The assessment conducted here suggests that codes and standards for Li-ion battery vehicle systems are in their early development stages and immature at this time. The assessment suggests there are gaps and risks inherent in new and rapidly evolving technology including

- Immature design and manufacturing standards,
- Immature safety systems integration requirements,
- Immature quality control requirements,
- Immature battery life cycle durability requirements,
- Immature crash and post-crash safety requirements, and
- Potential for intentional and unintentional misuse and abuse.

This report emphasizes codes and standards, rather than regulation. Industry codes and standards are important for NHTSA in that they complement the FMVSS and define industry consensus on minimum design and test requirements to achieve a desired level of safety, particularly for components and subsystems. Safety codes and standards provide a basis for sharing safety knowledge, understanding, and experience across an industry as technology is evolving. They provide a consistent level of safety across the industry regardless of experience and resources. Risks in new technology development can be mitigated through the aggressive pursuit of safety codes and standards that compel industry to establish a common understanding and consensus on safety strategies. Performance-based industry standards support the continued development and evolution of technology, and avoid constraining design and innovation. Performance-based codes and standards help avoid the deployment of incompletely validated and tested designs that might reduce safety and help ensure a level playing field for all developers and manufacturers.

Some potential strategies to mitigate the risks identified in the project include

- Development of codes, standards, and design qualification tests,
- Development of safety systems integration standards and performance-based tests,
- Development of comprehensive quality control requirements,
- Development of life cycle durability requirements for each system level,
- Development of crash and post-crash crashworthiness safety test requirements,
- Development of standards for onboard diagnostics to prevent and mitigate misuse and abuse safety hazards,
- Research to characterize cell-level damage initiation, growth, and critical size at failure,
- Research to characterize cell-to-cell and array-to-array failure propagation, and
- Research to develop damage detection and growth interruption methods.

These strategies are consistent with conclusions and recommendations from other authors. Doughty (2012) recommends

- Improve our understanding of failure modes,
- Develop better characterization tools, and
- Improve the safety of energy storage technologies.

The potential gaps identified here do not suggest that Li-ion battery vehicles or the technology is unsafe, but that the technology is still evolving such that there is not yet an industry consensus on system design and performance-based test methodologies. Individual manufacturers are expected to conduct their own due diligence safety testing and analysis, while the industry is working to develop a consensus. Li-ion battery vehicle technology is following an evolution of technology similar to that of alternative fueled vehicles from the late 1980s forward. In this stage of technology development, designs are evolving and highly proprietary, limiting the ability of industry members to publicly discuss their knowledge and insights.

Li-ion battery technology shows great promise for enabling substantial improvements in energy efficiency in mobile and stationary applications at modest cost. The technology is in the early stages of development. As with other high energy density storage technologies, failure of a Li-ion battery may release substantial amounts of energy that may create safety hazards. The investigation suggests that Li-ion battery safety can be managed effectively, although substantial research and development and codes and standards development is needed. In all cases, management of Li-ion battery safety requires insight, knowledge, and modeling of behavior, stress and performance at the electrochemistry level.

References

Doughty, D. H. (2012). Vehicle Battery Safety Roadmap Guidance (Report No. NREL/SR-5400-54404). Golden, CO: National Renewable Energy Laboratory. Available at www.nrel.gov/docs/fy13osti/54404.pdf

1 Introduction

With increasing public concerns about rising gasoline prices and climate change, battery electric, hybrid electric, and plug-in hybrid electric vehicles offer substantial promise of reducing fuel consumption and the impact of transportation on the environment, without the need for a large new alternative fuel infrastructure. While their use is promising, battery and hybrid electric vehicles also present significant engineering challenges. High-voltage battery vehicles must meet stringent safety requirements and yet achieve the driving range, reliability, and cost targets expected by consumers.

NHTSA promotes the safety of vehicles through several means, including setting and enforcing safety performance standards for motor vehicles and associated equipment through regulations such as those set forth in the Federal Motor Vehicle Safety Standards. Recognizing the unique hazards and issues associated with use of Li-ion battery vehicles, NHTSA is undertaking studies to determine if implementation of Li-ion batteries in vehicles may create potentially unsafe conditions and to determine if enhancements to the FMVSS may be necessary to ensure that Li-ion battery vehicles exhibit an equivalent level of safety to that of conventional drive train vehicles.

NHTSA has relied heavily on informational exchanges with vehicle manufacturers to learn of design strategies to mitigate onboard energy storage system hazards, and test data that verifies safe performance under prescribed crash conditions. NHTSA has also followed the development of industry standards and international regulations addressing the safety of these vehicles. The assessment presented here complements NHTSA's ongoing research efforts, providing an independent, structured assessment of safety performance requirements for Li-ion battery energy storage onboard vehicles.

1.1 *Project Objectives*

The work described herein was performed by Battelle in a Task Order under the NHTSA Engineering Assessment of Current and Future Vehicle Technologies Indefinite Delivery, Indefinite Quantity Contract DTNH22-08-D-00085. The objective of this Task Order was to provide NHTSA information it can use to assess needs and prioritize its future research activities on Li-ion battery vehicles. This analysis was intended to assist NHTSA in identifying potential critical operational safety issues it may want to consider and in assessing if further testing is needed to evaluate safety concerns.

The scope of this effort included plug-in hybrid electric vehicles, hybrid-electric vehicles, and battery electric vehicles. The effort takes into account propulsion system hazards and controls at the cell, module, pack, system, and vehicle level. The scope also considers operational conditions of charging (110V, 220V, 440V), driving, key-off, crash, and environmental exposure, battery aging, road induced shock, and vibration.

1.2 Purpose, Overview, and Organization of this Document

As noted above, the objective of this Task Order was to assess potential Li-ion battery vehicle safety issues and provide NHTSA information it can use to assess needs and prioritize its future research activities on Li-ion battery vehicles. This analysis is intended to assist NHTSA in identifying potential critical operational safety issues it may want to consider and in assessing if further testing is needed to evaluate safety concerns. This document is the comprehensive final report for the project, summarizing background, system design, analysis and observations and considerations. The purpose of this document is to compile and summarize, in a single document, the key background information and assessment results developed during the course of this investigation. This document is intended to provide a compendium of available technical background relevant to the safety of Li-ion battery systems for vehicles to inform NHTSA and to support its assessment of research and development needs.

Li-ion battery technology and vehicles are developing rapidly; a plethora of technical papers and commercial information are available on the internet. Much of the available information is focused on design of systems and less of it is focused on understanding safety and safety testing of these systems. This is partly because publication of safety research sometimes trails development of new technology and partly because commercial product developers must protect their proprietary interests. In addition, the data and information that are available are disparate and not organized to support the safety assessment needs of this project. Hence, the task to develop this material has focused on capturing a broad database of information, analyzing it and compiling it in a template that supports NHTSA's need for relevant safety information on Li-ion battery vehicles.

This report is organized into the following chapters and appendices.

- Chapter 2. Li-ion Cell Electrochemistry and Safety Performance
- Chapter 3. Li-ion Cell Design and Safety Performance
- Chapter 4. Li-ion Battery System Architecture
- Chapter 5. HEV, PHEV, and BEV Battery System Analysis
- Chapter 6. Battery Management and Control Systems
- Chapter 7. Battery Conditions That Enhance the Initiation and Growth of Internal Shorts
- Chapter 8. Overview of Relevant Safety Standards
- Chapter 9. Codes and Standards Comparison and Gap Analysis
- Chapter 10. Potential Hazards, Risks and Risk Mitigation Strategies
- Chapter 11. Summary of Observations and Considerations
- Appendix A. Survey of Li-ion Battery Vehicles.

This organization first describes the chemical components of Li-ion batteries, their electrochemical behavior, performance and safety. The subsequent chapter describes the design and construction of Li-ion battery cells from chemical components and their performance and safety. The next chapter describes the integration of Li-ion cells into modules, packs and, ultimately, battery systems used to support vehicle propulsion. Chapter 5 provides an overview of battery systems as used in various vehicle power configurations. Chapter 6 describes battery management systems that control charge and discharge and ensure safety during normal and abnormal operations. In these chapters, the Battelle Li-ion Battery Team developed a research

template, identified, collected, and organized source material, analyzed the material, and compiled this report.

Internal shorts are a major mode of Li-ion battery failure, and in at least one study, the most common mode. Chapter 7 focuses on the emerging issue of the role of side reactions that can lead to internal short circuits (shorts) and the influence of the operating conditions on the initiation and growth of these events. The initiation of these shorts can be the first step in a cascade that leads to thermal runaway and other safety and performance events. The purpose of this assessment is to provide information that can be useful in defining a simulated driving cycle suitable for safety testing of Li-ion batteries.

Industry standards have been developed to provide guidelines and qualification test requirements to help ensure the safety of Li-ion batteries for vehicles. Even as these standards have been published, industry has initiated development of enhanced versions because of the rapidly evolving developments in Li-ion battery technology. Safety standards are evolving rapidly but appear to trail—rather than lead—technology development. Chapter 8 summarizes the current published safety guidelines and requirements from key Society of Automotive Engineers standards for Li-ion battery vehicles.

Chapter 9 assesses potential gaps in design, manufacturing, and test standards intended to prevent or mitigate potential failure modes identified. A high-level approach was taken in this codes and standards gap analysis, in which Li-ion battery standards were compared to standards for hydrogen vehicle fuel systems as a benchmark of a mature set of industry standards. It represents automotive industry consensus on minimum design and test requirements to achieve the desired level of safety for onboard vehicle energy storage systems.

Chapter 10 integrates the results of the preceding chapters of the report to summarize potential hazards, risks, and risk mitigation strategies for Li-ion battery vehicle safety identified in the program. Chapter 11 provides a closing executive summary of observations and considerations.

Li-ion batteries are being implemented in a large number of vehicle propulsion systems, including battery electric, hybrid-electric, and plug-in hybrid electric vehicles. The Appendix summarizes available information on Li-ion battery vehicles, including speed, range, motor, and battery specifications.

Safety of Li-ion batteries and vehicles is a complex topic; safety features are implemented at the chemistry, cell, module, pack, and vehicle levels. Each chapter in the report discusses relevant safety topics, and there is some overlap and duplication. The authors have elected to allow overlap to ensure that relevant information is available for the reader who may desire to examine a single topic and not be required to read the entire report to capture desired information.

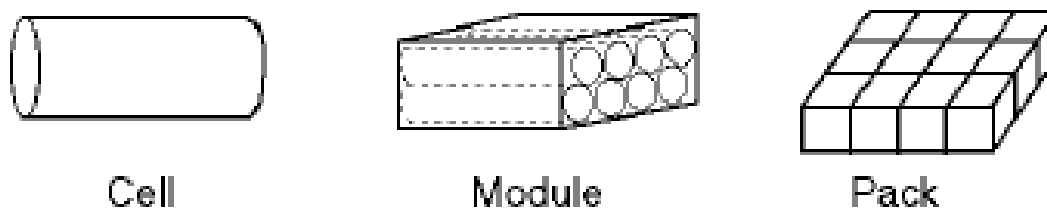
2 Li-ion Cell Electrochemistry and Safety Performance

Current vehicle manufacturers are developing and commercializing all-electric and range extended plug-in vehicles. These BEVs and PHEVs plug directly into the electrical grid to charge the propulsion battery. When compared to current commercial hybrid vehicles, which use a combination of battery and internal combustion engine, the BEVs and PHEVs require greatly improved battery systems. The improved battery systems need between 15 and 50 times the amount of energy storage and must allow for greater depth of discharge of the battery during operation. One of the leading battery types possessing the performance characteristics needed to enable the BEVs and PHEVs is lithium-ion.

The performance characteristics of large battery systems are determined by the basic electrochemistry that occurs at the interfaces of the system components at the cell level. The main electrochemical interfaces in the cell are between the anode, electrolyte, and cathode. The choice of the anode and cathode determines the voltage, capacity, and specific energy. The performance requirements of the automotive drive train that uses the Li-ion battery will determine what specific embodiment of the battery is needed. This section of the report discusses Li-ion battery electrochemistries that are available or in development that might be considered for Li-ion battery vehicles. This section also identifies candidate materials used for the anode, cathode, and electrolyte and their electrochemical interactions, and it describes electrical performance of different cell chemistries and failure modes and hazards at the electrochemical level.

2.1 Li-ion Cell Components

A “cell” is the fundamental building block of an electrochemical system. Cells are built up to battery modules, and modules are built up to battery packs and battery systems, as illustrated in Figure 2-1.



Source: Gaines and Cuenca, 2000. Reprinted with permission.

Figure 2-1. Illustration of a cell, a module, and a whole battery system (pack).

When compared with other battery chemistries, especially those that are also used for electric vehicles, Li-ion batteries provide many advantages and some disadvantages, outlined in Table 2-1 (Reddy & Linden, 2011).

Individual Li-ion cells are manufactured in several different configurations, including cylindrical, prismatic (both wound and flat plate), pouch, and large format cell designs, described in the next chapter. Regardless of configuration, cells are made up of the following subcomponents.

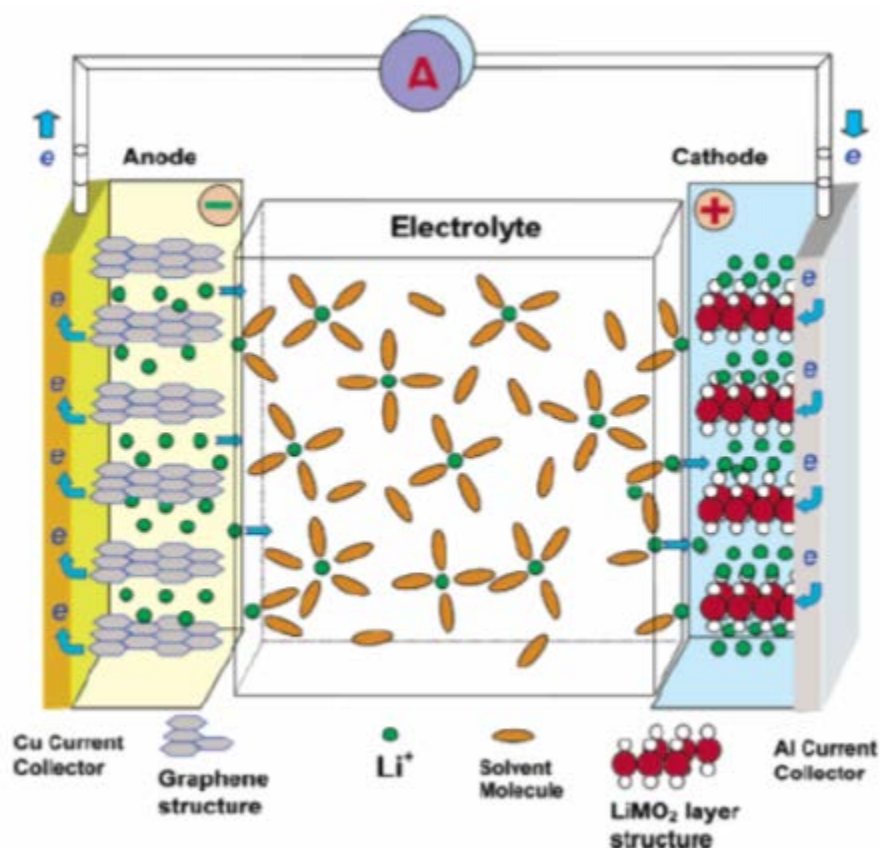
- Cathode: positive electrode; accepts electrons during battery discharge
- Anode: negative electrode; gives up electrons during battery discharge
- Electrolyte: transfers ions between the anode and cathode
- Separator: solid material between the anode and cathode that serves two roles:
 - Prevents internal short circuiting between the anode and cathode by preventing direct electron flow from the anode to the cathode
 - Provides a path for ionic conduction in the liquid electrolyte within the interconnected porous structure of the separator

For each subcomponent, there are numerous variations both in commercially available cells and those still under research. Each combination of cathode chemistry, anode chemistry, electrolyte composition and additives, and separator type provides a range of power densities, charge regimes, capacities, charge management techniques, and safety concerns and challenges.

Table 2-1. Summary of lithium-ion battery advantages and disadvantages.

Advantages	Disadvantages
<ul style="list-style-type: none"> • Sealed cell—no need to replace electrolyte • Long cycle life • Long shelf life • Ability to be charged quickly • Ability to be discharged with a high rate and high power • High specific energy and energy density • No memory effect, unlike nickel-cadmium • Numerous variations on cathode, anode, and electrolyte chemistry provide basis for design flexibility 	<ul style="list-style-type: none"> • Higher cost than more traditional batteries (e.g., NiCad and NiMH) • Degradation at high temperatures • Potential for thermal runaway or capacity loss when overcharged, causing excessive Li extraction from cathode and excessive insertion at the anode, leading to less thermally stable electrodes • Instability when charged too quickly at low temperature (<0°C) • Need for complex management circuitry in multi-cell modules to prevent the above disadvantages from leading to safety hazards

During battery operation (i.e., charging and discharging), ions move back and forth between the cathode and anode through the electrolyte, and electrons move through the external circuit. During cell discharging, the anode oxidizes (loses electrons) and the cathode experiences a reduction (gains electrons). While this is occurring, Li⁺ ions are transferred through the electrolyte from the anode to the cathode. During charging, this process is reversed. The electrochemical process that occurs during charge and discharge is an “intercalation” process, in which Li-ions become temporary “guests” to the host electrodes without any major structural change to the electrodes. The majority of what happens during this process is reversible; however there is potential for some irreversible change, such as stress-induced damage, that occurs with each discharge and charge cycle. Figure 2-2 illustrates the reaction mechanism (Xu, 2004; U.S. DOE, 2007).



Source: Xu, 2004. Reprinted with permission.

Figure 2-2. Pictorial representation of a Li-ion cell during discharge.

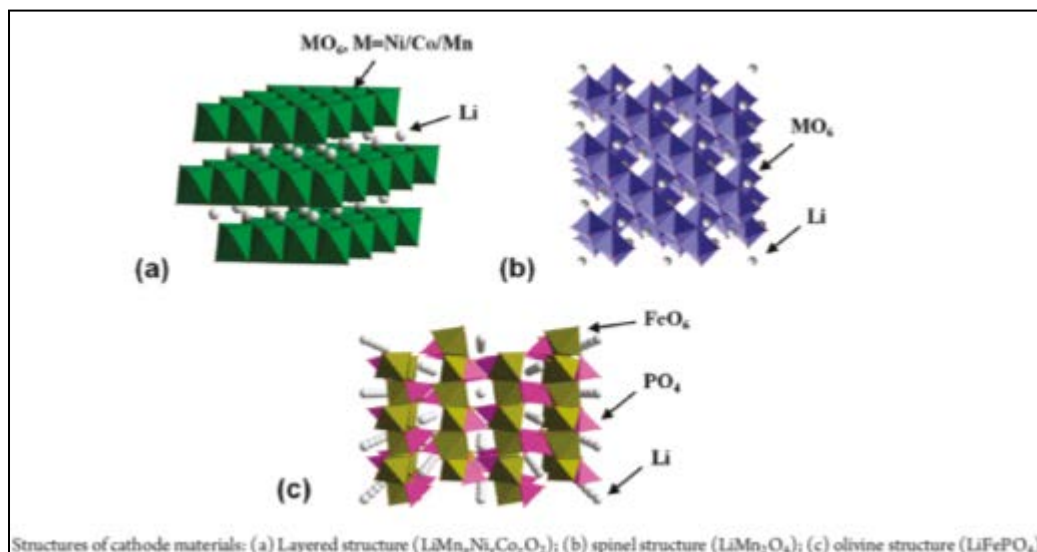
2.1.1 Cathode

A cathode in an electrochemical cell accepts electrons and ions during discharge of a cell. The active material of a cathode in a Li-ion cell is made from a combination of a lithium metal oxide or lithium metal phosphate, a polymer binder (polyvinylidene fluoride [PVDF], carboxymethylcellulose or styrene/butadiene rubber) and conductive filler (carbon black). These materials are made using standard inorganic material manufacturing processes. The active materials adhere to a metallic current collector (Reddy & Linden, 2011). Coatings on the electrodes are sometimes used to lessen the occurrence of internal shorting. In the majority of instances, the cell assemblers are not the manufacturers of the raw materials in the cell.

For a material to be a candidate for use as the active cathode material, it must possess the following attributes.

- A high potential when compared to lithium metal potential
- Ability to reversibly insert and remove lithium without change in structure
- High Li-ion diffusivity through its matrix
- Good electrical conductivity
- Chemical resistance against solubilization by the electrolyte and its additives
- The ability to be manufactured from low-cost starting raw materials.

There has been extensive research to identify, in several crystal classes, new chemistries that can be used for the active material in a cathode for the Li-ion cells. The structure of the materials is important because it is what drives the cathode's ability to accept lithium-ions during the electrochemical reactions. There are generally three molecular structure types of cathodes commercially available, including: (1) an ordered or layered, rock salt type of structure; (2) a spinel-type structure; or (3) an olivine-type structure. These molecular structures are illustrated in Figure 2-3 (Yang et al., 2011).



Source: Reprinted with permission from Yang et al. *Chemical Reviews* 111 (5): 3577-3613, Fig. 28. Copyright 2011 American Chemical Society.

Figure 2-3. Molecular structure of cathode materials.

In addition to the intrinsic chemistry, the size, shape, distribution, and density of the crystals also contribute to cell and battery performance. Table 2-2 summarizes background information on current cathode chemistries in use or under research today.

Table 2-2. Overview of Li-ion cathode chemistries.

Structure	Cathode Type	Chemistry	Details
Layered	Li-Cobalt LCO (Lithium Cobalate)	LiCoO_2	The majority of portable chemistries use this cathode material, along with a graphite carbon anode. This combination provides for high energy density and a long run time. However, the chemistry provides a relatively low discharge current. It has been reported that, after 24 to 36 months of cycling, the pack often becomes unserviceable due to a large voltage drop under load that is caused by high internal resistance (Battery World, 2012).
	Lithium Nickel Cobalt Aluminum Oxide NCA	LiNiCoAlO_2	Reports suggest that NCA is somewhat safer than LiCoO_2 , largely by virtue of the fact that it has a slightly lower voltage at full charge and therefore a larger margin to accept overcharge. It has been further suggested that NCA also has far superior life characteristics, both on float and in cycling, and is therefore the positive material of choice for many automobile manufacturers for the next generation of hybrid electric vehicles (McDowall, 2008).
Spinel	Li-Manganese LMO (Lithium Manganate)	LiMn_2O_4	The manganese possesses a three-dimensional spinel structure that improves the ion flow between the electrodes. High ion flow lowers the internal resistance and increases loading capability. The resistance stays low with cycling; however, the battery does age and the overall service life is similar to that of cobalt. It has been reported that Spinel has an inherently high thermal stability and needs less safety circuitry than a cobalt system (Battery World, 2012). Low internal cell resistance is the key to high rate capability. One of the shortcomings of this system is the lower capacity compared to the cobalt-based system. Spinel provides a capacity that is about half that of the cobalt equivalent. But, spinel still provides an energy density that is about 50% higher than that of a nickel-based equivalent.
	Lithium Nickel Manganese Cobalt NMC	LiNiMnCoO_2	Tends to be more stable, and therefore more resistant to overcharging, than LCO. Rapidly loses capacity through cycling.
	Lithium Nickel Manganese Oxide	$\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$	Its primary advantage is that it can reach an operating voltage of 5V, which leads to a significant increase in energy density. An obstacle to its practical use is that organic carbonate electrolytes typically used in Li-ion batteries are not compatible with voltages approaching 5V (Scrosati & Garche, 2010).
Olivine	Li-Phosphate LFP (Lithium Iron Phosphate)	LiFePO_4	Exception to the rule that a cathode material must have high ionic and electronic mobility. This material achieves adequate lithium transport by using electrode materials with nano-sized particles. For a significant improvement in safety in a positive electrode material, it has been suggested to move away from oxide materials to ones based on phosphates. Phosphate bonds are much stronger than those in oxides, with the result that when abusively overcharged, LiFePO_4 cells release very little energy. Cells using LiFePO_4 have reasonable calendar life and excellent cycling characteristics as long as they are operated at moderate temperatures. It has been further suggested, however, that there is a tradeoff between the added safety and lower energy density (McDowall, 2008).

2.1.2 Anode

An anode in an electrochemical cell loses electrons and ions during the discharge of the cell. The anodes in Li-ion cells are typically carbon-based materials. A wide variety of carbons are used as negative electrodes today. Common forms include graphene, graphite, and carbon black. These forms can be oriented as planar, whiskers, or spherules. Graphite is one of the most commonly used anode materials. It stores lithium well within its structure and maintains stability over a long cycle life.

As a historical background note, secondary (rechargeable) lithium batteries in years past used lithium metal negative electrodes due to their high specific capacity. However, this type of anode is susceptible to formation of dendrites, hard metallic lithium deposits that form on electrode surfaces and may continue to grow until they penetrate the separator and cause an internal electrical short, rapid increases in cell temperature, and thermal runaway. A large number of rechargeable metallic anode lithium batteries were recalled in Japan in 1990 due to serious failures (Nagura & Tozawa 1990). These issues are not as common today when using carbon-based anode chemistries, which provide a much more stable surface morphology.

2.1.2.1 Solid electrolyte interface (SEI) Layer

During the first cycle in Li-ion batteries, a semi-permanent coating layer is formed on the anode and cathode, called the solid electrolyte interface (SEI). This layer is a significant enabling feature of Li-ion technology. This is because the graphite electrode potential is so negative that the Li-ions between the carbon layers would be expected to react immediately with the solvent of the electrolyte. The SEI is permeable to Li-ions but not to the electrolyte, and its stability is an important requirement for long operating life.

There is high electrochemical reactivity between the Li-ion electrode materials of composition and the non-aqueous electrolytes at high cell voltages. This is the reason for many of the current concerns and recent historical safety issues and incidents. The reactivity can be suppressed and countered by the formation of the SEI layer in commercial devices. The battery performance potential is sometimes hindered, however, because of the safety devices required at the cell, module, and system level.

In some instances, lithium titanate is used as the active material in the anode. It has a less negative voltage than the graphite anodes. This enables the Li-ions to be more stable and less likely to react with the electrolyte. For lithium titanate, no SEI is formed and the cell is more stable at higher voltages.

Table 2-3 outlines some of the anode materials in use or under development. The majority of cells use a carbon based anode, and the other three outlined are still primarily in the research phase of development.

Table 2-3. Overview of Li-ion anode chemistries.

Anode Type	Chemistry	Details
Carbon	$C \rightarrow C_xLi_x$	The most common form of anode, carbon electrodes provide a stable surface morphology that stores lithium well within its structure and maintains stability over a long cycle life. A wide variety of carbons are used as negative electrodes today. Common forms include graphene, graphite, and carbon black. These forms can be oriented as planar, whiskers, or spherules.
Lithium Titanate LTO	$Li_4Ti_5O_{12}$	Lithium titanate negative material operates at a higher (less negative) voltage, at which Li-ions are stable with respect to the electrolyte. The higher negative electrode voltage leads to lower cell voltage, so energy and power density suffer accordingly. An SEI does not form and the overheating problem (for the anode) is eliminated, allowing cells to be charged at a much higher rate, sometimes in as little as 5 minutes. (McDowall, 2008)
Sn-Co-C ternary alloy		Scrosati and Garche (2010) suggest that this material is already in use as an anode material in a commercial battery.
Silicon	Si	Silicon achieves a 20 to 30% increase in specific energy at the cost of lower load currents and reduced cycle life due to the large volume change upon lithiation (Munao, van Erven, Valvo, Garcia-Tamayo, & Kelder, 2011; Oumellal et al., 2011).

2.1.3 Electrolyte

The electrolyte is the physical medium that allows ionic transport between the electrodes during charging and discharging of a cell. Electrolytes in Li-ion batteries may either be a liquid or a gel. Lithium batteries use non-aqueous electrolytes because of reactivity of lithium with aqueous electrolytes and the inherent stability of non-aqueous electrolytes at higher voltages. Liquid electrolytes are a combination of a solution of solvents and lithium salts, as well as additives that improve the cell performance. The liquid electrolyte in Li-ion cells is typically lithium hexafluorophosphate ($LiPF_6$) dissolved in a mixture of organic solvents (mainly carbonates), which must be formulated to match the electrode materials used. With gel electrolytes, also known as lithium polymer cells, a monomer is added to the electrolyte during the assembly of the cell and is thermally activated. This reaction creates a polymer electrolyte that encompasses the entire internal geometry of the cell.

For example, a cobalt-based cell has a full-charge voltage of 4.2 V and the electrolyte must be able to withstand this voltage; the resulting electrolyte formulation could be quite different from that of a lower-voltage phosphate-based cell. Certain electrolyte constituents can also contribute to stabilization of the SEI, and vinylene carbonate is particularly effective in this regard. The electrolyte composition may also be fine-tuned to operate at lower or higher temperatures. The electrolyte in consumer cells often includes so-called overcharge additives. These are compounds that are intended to decompose during moderate overcharge, producing gas that increases internal cell pressure and causes an internal circuit breaker to open, thus sacrificing the cell but preventing further overcharge. In floating operation, however, there is evidence that overcharge additives can polymerize in normal operation, causing a dramatic increase in cell impedance.

The electrolyte must be able to accept a high salt concentration, be functional across low and high temperature operating conditions, and must be non-reactive. The reactivity of electrolyte systems (solvents, salts, additives) has been well studied, and must be taken into account with any discussion of systems safety in Li-ion battery systems. Fuller explanations of previous scientific research in this area can be found in Harris, Timmons, and Pitz (2009).

2.1.3.1 Solvents

A common solvent used in Li-ion cells is a combination of ethylene carbonate and dimethyl carbonate (Xu, 2004). EC allows for very effective formation of the required SEI layer on the carbonaceous anode, and it has a high dielectric constant, which gives it the ability to dissolve a wide variety of Li salts. EC has a higher melting point ($\sim 36^{\circ}\text{C}$) than DMC and is solid at room temperature. DMC (and other linear carbonates) are liquid at room temperature, and have a low viscosity, which leads to higher ionic conductivity. DMC can be mixed with EC to lower the melting point of EC to below room temperature, resulting in a liquid electrolyte. The liquid mixture possesses the merits of each component: (1) strong formation of the SEI layer (EC); (2) high solvation power of lithium salts (EC); and (3) low viscosity and high ionic conductivity (DMC).

Propylene carbonate is another solvent that has been investigated for Li-ion cells. PC has a high dielectric constant, which gives it the ability to dissolve a wide variety of Li salts. PC has some ability to form the SEI layer, but it is not as effective as EC. This lesser ability to protect the SEI layer leads to poor cycling efficiency.

2.1.3.2 Salts

A common salt used in Li-ion batteries is lithium hexafluorophosphate (LiPF_6) (Xu, 2004). LiPF_6 has a combination of well balanced properties, such as ionic conductivity, thermal stability, anodic stability, chemical stability toward ambient moisture, and dissociation constant. The common combination of EC/DMC solvent mixture with LiPF_6 salt enables Li-ion batteries to deliver their rated capacity and power up to 50°C . At higher temperatures, reactions between the solvent and salt can produce gaseous products that lead to hazardous pressure build-up (Xu, 2004).

Other salts have been researched, but they are not typically used in commercial cells. Lithium hexafluoroarsenate (LiAsF_6) is toxic, and is never used in commercial cells. Lithium tetrafluoroborate (LiBF_4) has inferior ionic conductivity. Lithium trifluoromethanesulfonate (LiTf) leads to corrosion of the aluminum current collectors. Lithium bis(trifluoromethanesulfonyl)imide (LiIm) also leads to corrosion of aluminum current collectors. Lithium perchlorate (LiClO_4) is a strong oxidant, which makes it impractical to use for industry purposes.

The salt LiBOB ($\text{LiB}(\text{C}_2\text{O}_4)_2$) is less acidic than LiPF_6 , and it has been found to be more stable than LiPF_6 when used with lithium manganese oxide, “manganese spinel” cathode material (Ritchie & Howard (2006)). However, solutions containing lithium bis(oxalato)borate (LiBOB) are less conductive than those containing LiPF_6 . This results in lower performance at higher charge and discharge rates.

2.1.3.3 Electrolyte Additives

Additives play a role in modifying anode reactivity, reducing electrolyte flammability, and retarding electrolyte decomposition. It has been reported that the salt LiPF_6 reacts with the EC/DMC solvent at temperatures greater than 50°C (Xu, 2004). The addition of Lewis base additives has been found to retard this electrolyte decomposition, leading to the ability to run Li-ion batteries higher than 50°C (Ritchie & Howard, 2006).

Overcharge protection can be provided by additives that decompose at a cell voltage slightly above the normal operating voltage of the cell. If any overcharging occurs, the additive decomposes into a gas, which causes internal pressure to rise, which in turn trips a mechanically activated internal circuit breaker that disrupts the flow of charge.

2.1.3.4 Li-ion Gel/Polymer Electrolyte

Solid electrolytes (ceramic and polymeric) can lead to improved safety because they eliminate the possibility of flammable liquid electrolyte solvent leaking from an unsealed cell. Solid electrolytes generally have the disadvantage of having lower ionic conductivity than liquid electrolytes, which results in lower power output. A number of different solid electrolytes have been investigated. Gelled polymers that have shown the highest conductivities include $\text{Li}_{1-x}\text{Al}_x\text{Ge}_{2-x}(\text{PO}_4)_3$ (LAGP) and poly(vinylidene fluoride)-hexafluoropropylene (PVdF-HFP). However, these have some disadvantages over other potential solid electrolytes, such as lower mechanical strength or reduced electrode compatibility.

There are several examples of solid electrolyte types for Li-ion batteries. Poly(ethylene oxide) hosting a lithium salt is one example of the many polymer-based electrolytes that have been investigated (Scrosati & Garche, 2010). A practical problem in using this solid electrolyte is that its ionic conductivity is high only at temperatures above 70°C . It has been reported that LiPON (lithium phosphorus oxinitride) is a solid electrolyte that is already in use in Li-ion micro batteries (Knauth, 2009). Overall, conductivity using this type of electrolyte may be too low for use in automotive applications.

2.1.3.5 Ionic Liquids

Room-temperature ionic liquids are salts with low-temperature melting points, which can be used as electrolytes in electrochemical devices. These room-temperature ionic liquids have a low vapor pressure. This contributes to low flammability levels (Lewandowski & Swiderska-Mocek, 2009), which would give them potential for improving the safety of Li-ion batteries. In general, their high viscosity gives them an ionic conductivity that is lower than typical liquid electrolytes, which leads to lower power output. It is not clear how well ionic liquids can promote the formation of the SEI or to what extent they require SEI formation. Cost is still high at this point, and batteries that use ionic liquids generally are not yet commercially available.

2.1.4 Separator

The separator is a microporous, electrically insulating material that is positioned between the anode and the cathode. The separator performs two critical roles (Huang, 2011). First, it prevents internal short circuiting between the anode and cathode by providing a physical, non-electrically conductive barrier. Second, it provides a path for ionic transport.

There are two different common types of separator: Freestanding micro porous films and polymer or gel separators/electrolytes. There are also “solid” (or pseudo-solid) separators/electrolytes, but these are used in only specific chemistries/constructions. The types of separators used in different types of secondary lithium batteries are shown in Table 2-4.

Table 2-4. Lithium / Li-ion battery constructions.

Battery System	Type of Separator	Separator Material
Lithium-ion ("liquid electrolyte")	Microporous	Polyethylene, polypropylene, and other free standing separators
Li-ion "gel polymer"	Microporous	Poly vinylidene difluoride or polyethylene, polypropylene, or their laminates coated with PVDF or another laminating or bonding layer.
Lithium polymer (such as Li-V ₆ O ₁₃)	"Solid" Polymer electrolyte	Poly ethylene oxide (either solvated with an electrolyte or in the melt state) with lithium salt, often with additional cross-linkable polymer.

Source: Adapted from Arora ., & Zhang, 2004

There is no official definition of “liquid,” “gel polymer,” or “polymer” systems or structures. The difference is at best subtle. Today, a reasonable—although not widely accepted—differentiation is that the “gel polymer” or “polymer” separator/electrolyte produces an integrated, bonded system generally of a single polymer chemistry where the free standing separator requires mechanical means of holding the electrodes together. (In cylindrical cells, the winding holds the elements together. Prismatic cells normally rely on a vacuum within the cell and use atmospheric pressure to hold them together until they are assembled into a battery and restrained.) Manufacturers have further blurred the distinction because the “liquid” electrolyte connotation carries a old stigma of flammable liquid electrolyte leaking out. And the term “gel polymer” has been supplanted by the term “polymer.”

Free standing separators are generally polyolefinic micro porous membranes. There are two processes of manufacture: a wet process and a dry process. All of these rely on an electrolyte absorbed into the pores. The pores are of such size and structure that most if not all of the electrolyte is well retained and does not drain out. However, some large capacity batteries may have an appreciable amount of free, liquid electrolyte within the cell case (Mikolajczak, Kahn, White, & Long, 2011).

The “classic” gel polymer or polymer separators/electrolytes trace back to the Bellcore technology and are generally based on a layer of micro porous PVDF with absorbed electrolyte, laminated to one or both of the electrodes. Today the term “polymer” is often used to include any laminated cells and even cells of the classic “liquid” construction.

The “solid polymer” separators/electrolytes are generally employed in lithium metal cells. Most of them are based upon polyethylene oxide or derivatives. PEO does not have an acceptable ionic conductivity at room temperature (where it exists as a solid) and can either be swollen with an electrolyte or operated at elevated temperatures (like the previous AVESTOR technology). In the swollen or molten state, the separator has very little compressive strength. As a result, modifications today involve adding a cross-linkable polymer system, effectively making these systems for all intents and purposes micro porous.

There are also inorganic solid separators for solid state batteries. These rely on ionic migration through an extremely thin glass such as thiolysicon. Such systems have not yet been scaled up for large commercialization.

A good separator must have the following properties:

- Good electrical/electronic insulator
- Minimum contribution to ionic resistance
- Adequate mechanical properties
 - Sufficient strength and elongation to not fail in deformations caused by U.N.38.3 bar crush test and other abuse testing
 - Sufficient physical strength without “neck-down” to allow easy handling
 - Good puncture resistance to prevent debris particles from creating a short circuit or wearing through under constant flexing and later creating a short circuit
 - Good compression resistance so as not to create a hole and short under point pressure
- Chemical resistance to degradation by electrolyte, impurities, and electrode reactants and products
- Readily wetted by electrolyte
- Uniform in thickness and other properties.

A separator material must first be an adequate electronic insulator to prevent a short circuit between the electrodes. Ideally, the separator will not decrease the ionic conductivity of the electrolyte, although in practice ionic conductivity is always decreased by the presence of a separator. Generally, a thin membrane with high porosity will minimize the decrease in ionic conductivity.

The thickness of the membrane and the amount of porosity must be balanced with the mechanical strength of the material to avoid having a separator that easily tears or forms holes or has electrical leakage or self discharge. The formation of large holes in the separator will allow the electrodes to contact, leading to a short circuit and thermal runaway. Separators are part of a dynamic system, as the anode and cathode both expand and contract as Li-ions move from one to the other. Since the anode and cathode do not necessarily expand and contract in balance, there is constant compressing and releasing of the separator. Further, in cylindrical cells, there is constant stretching and relaxing. This constant abuse can cause particles of debris, not apparent in the initial formation, to wear through and cause a short, thus driving the demand for puncture resistance. The separator must also have reasonable elongation, as a U.N.38.3 bar crush test will cause a large dent in the side of a large cylindrical cell. If the separator does not have sufficient elongation, it can split and allow a short to occur.

The separator material must also be stable in the electrolyte during operating conditions. It must not react with or dissolve in the electrolyte that is used, and it must be chemically and electrochemically stable when in contact with the anode and cathode at the electrical potentials expected to be encountered. The separator must also be able to withstand the temperature that is present in normal operating and storage conditions including anticipated abuse conditions (such as sitting on the dashboard of a closed car sitting in the sun). This means not only not melting, but also not shrinking where the edges of the separator could shrink to within the perimeters of the electrodes, allowing a short to occur.

Table 2-5 (Huang, 2011) provides a list of common commercial separators, which are typically made of porous polyolefin membranes.

Table 2-5. Commercially available microporous separators.

Manufacturer	Material	Separator Orientation
Asahi Kasei Chemicals	Polyolefin and ceramic-filled polyolefin	Biaxial
Celgard LLC	Polyethylene, polypropylene, possibly laminated	Uniaxial
Entek Membranes	Ceramic filled ultrahigh molecular weight polyethylene	Biaxial
ExxonMobil Tonen	Polyethylene and mixtures of polyethylene and polypropylene	Biaxial
SK Energy	Polyethylene	Biaxial
Ube Industries	Laminated polypropylene, polyethylene, polypropylene	Uniaxial

Source: Huang, 2011. Reprinted with permission.

In addition, DuPont is developing Energain Separators for high-performance Li-ion batteries and capacitors that are claimed to have low ionic resistance and high temperature stability. Energain is a polyimide based nanofiber product stable in Li-ion battery electrolytes. The product is a web of continuous filaments with diameters between 200 and 1,000 nanometers. This new separator technology is touted as having improved abuse tolerance, which would lead to improved safety.

Separators are often designed to have “thermal shutdown” capability to improve the safety of Li-ion cells. Upon reaching a temperature above the normal operating temperature of the cell, the separator can flow and fuse into a continuous film as the pores collapse. Once the pores are closed, the conduction of ions ends, and the cell is disabled, which presumably prevents some further reactions that can cause thermal runaway.

Separators that consist of a layer of PP and PE have been designed to reach an improved combination of thermal shutdown ability and melt resistance. In this layered design, at temperatures in the range of 120 to 150°C, the porous PE layer will melt and fill/blind the pores of the higher melting point PP layer, while the PP layer maintains its mechanical integrity and keeps the electrode separated.

The thermal shutdown temperature of polypropylene is around 160°C, and the thermal shutdown temperature of polyethylene is between 120 and 150°C. Ideally, the difference between the shutdown temperature and the melting temperature should be as large as possible. This will prevent a situation where a rising internal cell temperature reaches the pore blinding temperature, and quickly continues up to the melting temperature. If the separator melts, holes may form that could lead to contact between the electrodes. This short circuit may cause thermal runaway and possibly casing rupture and secondary fire.

There is a potential hazard in the shutdown separator concept: when a cell is shut down – there is no longer any way to discharge the cell safely. The lithiated anode in cells that are fully charged could spontaneously burst into flame if exposed to the moisture in the air.

Table 2-6 further summarizes the relationship between important cell behaviors and desirable separator properties.

Table 2-6. Desirable Cell Behaviors and Relevant Separator Properties.

Cell Behavior	Separator Property	Relationships
High Storage Capacity	Less Thickness	Thinner separators permit greater cell capacity.
Low Internal Resistance	Less thickness, larger pore size, increased porosity, and lower tortuosity	Lower internal resistance improves the cell's energy efficiency and its performance at high charge and discharge current. Lower internal resistance also decreases internal heating during charge and discharge.
High-Temperature Storage	Chemical and thermal stability	Separator should remain chemically inert and structurally unchanged under the full range of storage conditions.
Control of Self Discharge	High electrical resistance. No thin areas, pinholes, or contamination by conductive species.	Internal paths for current flow increase current leakage.
Long-Term Cycling	Low ionic resistance, high chemical and mechanical stability	Separator should remain unchanged under the full range of operational conditions.
Resistance to Overcharge*	Present separators have no mechanism that can protect against overcharge	When the cell is overcharged, it is desirable for the separator to stop lithium transport to the anode.
Resistance to External Short Circuit	Automatic and reversible pore closure shutdown behavior	Desirable for the separator to shut down without melting to stop excessive current flow and resultant overheating. Desirable for the separator to allow ion transport after the external short is removed.
Resistance to High-Temperature Exposure**	High melting point	A melting point in excess of 200°C or sufficient ceramic filler is essential for the separator to keep the two electrodes mechanically and electrically separated at high temperature.
Resistance to Crush	High mechanical integrity	The separator must not split or rupture during deformations associated with crush to keep the anode and cathode mechanically and electrically separated.
Resistance to Puncture (nail penetration)	Present separators have no mechanism that can reliably protect against a hard short as caused by a nail penetration	Desirable for the separator to isolate the short before the current rush causes localized overheating
Resistance to Internal Short Circuit	Present separators have no mechanism that can reliably protect against an internal short	Desirable for the separator to isolate the short before the current rush causes localized overheating
Protection on Rupture	Laminated to anode to reduce moisture migration to anode surface	Adequate adhesion to remain bonded when cell is torn open to prevent reactions at the anode surface

*Overcharging is an electrical phenomenon. The result is an exothermic electro-chemical reaction between the electrolyte and the cathode.

**Shrinkage issues are important for separators when it comes to safety and Li-ion battery failure. For example, shrinkage in the transverse direction can lead to safety issues because of an internal short between the electrodes. (Adapted from Arora & Zhang, 2004)

A review article by Orendorff (2012a) explains the unique needs for separators in large cells.¹ The temperature variation across a cell can lead to non-uniform shrinkage of the separator. In many cases, large format cells use a shutdown separator to increase safety. However, if the temperature variation across the cell leads to only a part of the separator shutting down, then the current is forced through the remaining separator and accelerates the cell's failure. Orendorff et al. (2012b) summarize research to develop new separators.

2.2 Li-ion Cell Electrochemical General Characteristics and Performance Comparisons

General performance characteristics of Li-ion cells using common chemistries is outlined in Table 2-7 (Reddy & Linden, 2011) below. As can be seen in this table, the voltage between the cathode and anode ranges from 1.5 to 4.2 V, averaging 2.3 to 3.7 V. This higher voltage allows for the use of fewer cells to attain a desired voltage, which generates very high specific energy and energy density, up to 240 Wh/kg and 640 Wh/L, respectively. Additionally, these cells can perform across a broad range of temperatures: -20 to 45 C (charging temperature range) and -20 to 60 C (discharging temperature range). The exact characteristics and performance of Li-ion cells depend on the specific chemistry used. This section and table discusses only the most common of chemistries encountered today.

Table 2-7. General Performance Characteristics of Li-ion Cells (Cylindrical, Prismatic, and "Polymer") Using Common Cell Chemistries.

Characteristics	LiCoO ₂ /Graphite NMC/Graphite NCA/Graphite Energy Cells	NMC/Graphite LMO/Graphite Power Cells	LiFePO ₄ / Graphite Power Cells	LMO/Li _{4/3} Ti _{5/3} O ₄
Voltage range (V)	2.5-4.2 typ. 2.5-4.35 for some cells	2.5-4.2	2.5-3.6	2.8-1.5
Avg. Voltage	3.7	3.7	3.3	2.3
Specific energy (Wh/kg)	175-240 cylinder 130- 200 polymer	100-150	60-110	70
Energy density (Wh/L)	400-640 cylinder 250-450 polymer	250-350	125-250	120
Continuous rate capability (C)	2-3	Over 30	10-125	10
Pulse-rate capability (C)	5	Over 100	Up to 250	20
Cycle life at 100% DOD (to 80% capacity)	500+	500+	1000+	4000+
Calendar life (yr)	>5	>5	>5	>5
Self-discharge rate (%/month)	2-10 %/mo	2-10 %/mo	2-10 %/mo	2-10 %/mo
Charge temperature range (°C)	0-45 Some cells have wider range	0-45 Some cells have wider range	0-45 Some cells have wider range	-20-45 Some cells have wider range

¹ If a cell is of sufficient size that the conditions such as state of charge or temperature vary across it and cannot be assumed to be uniform, then it is termed a "large" cell or "large format" cell.

Characteristics	LiCoO ₂ /Graphite NMC/Graphite NCA/Graphite Energy Cells	NMC/Graphite LMO/Graphite Power Cells	LiFePO ₄ / Graphite Power Cells	LMO/Li _{4/3} Ti _{5/3} O ₄
Discharge temperature range (°C)	-20 to 60	-30 to 60	-30 to 60	-30 to 60
Memory effect	None	None	None	None
Power density (W/L) (pulse)	~2000	~10000	~10000	~2000
Specific power (W/kg) (pulse)	~1000	~4000	~4000	~1100

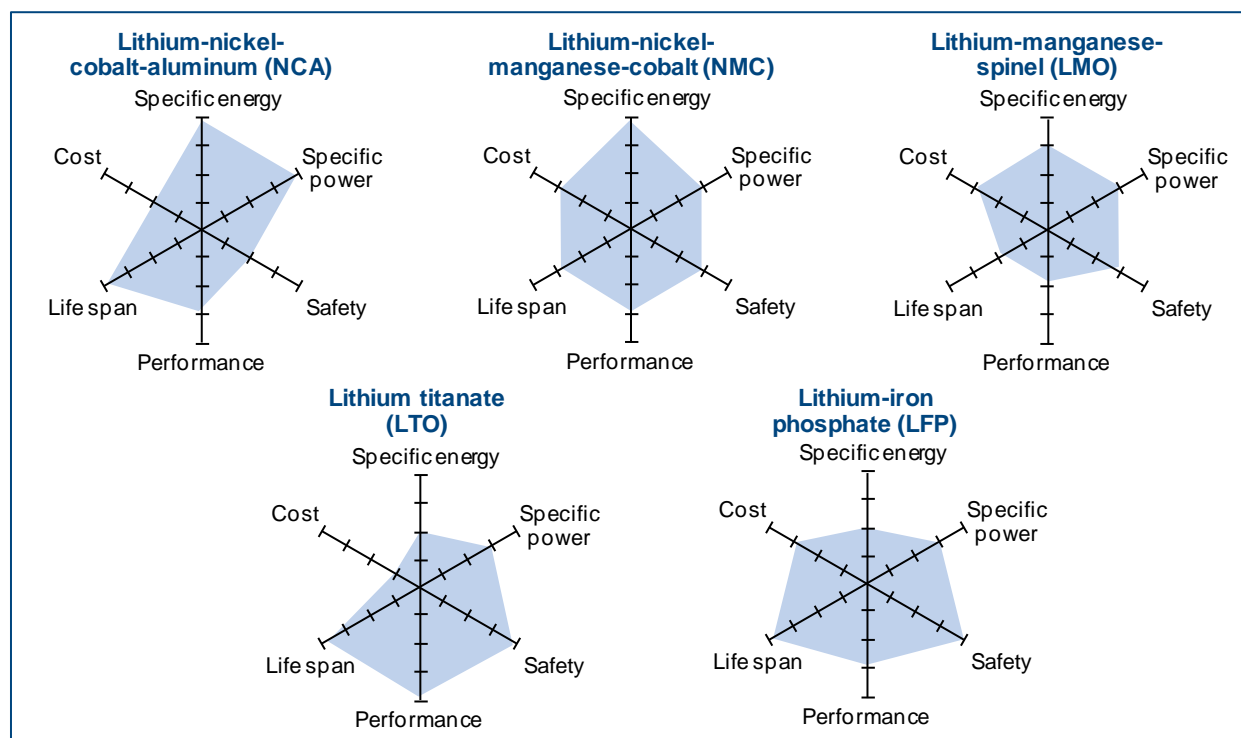
NMC = LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂, LiNi_{0.5}Mn_{0.3}Co_{0.2}O₂ or LiNi_{0.42}Mn_{0.42}Co_{0.16}, etc.

NCA = LiNi_{0.8}Co_{0.15}Al_{0.05}O₂, etc.

LMO = Li_{1+x}Mn_{2-x}O₄, etc.

Adapted from Reddy & Linden, 2011. Reprinted with permission.

Figure 2-4 (BCG, 2010, pg. 3) shows how the major battery chemistries compare graphically. There is much more to cell performance and safety attributes than basic chemistry parameters; this graphic provides the reader with a simplistic, but useful, illustration of tradeoffs that must be considered for different Li-ion battery designs, in a single snapshot.



Source: Boston Consulting Group, 2011. Reproduced with permission.

Figure 2-4. Relative comparisons of Li-ion battery performance parameters.

Research into improving the details of all of the components of the Li-ion cells continues. One such avenue is Li-air cells, where lithium metal acts as the anode and air acts as the cathode (Scrosati & Garche, 2010). The interest in this type of cell is the potential for a high specific energy on the order of 1,200 mAh/g. A key safety issue with this cell is that even traces of water can strongly react with the lithium anode. There are other difficulties with this cell in terms cost and rechargeability.

Li-sulfur cells have a high theoretical energy density of 2500 Wh/kg (Scrosati & Garche, 2010). A major issue with this cell design is that polysulfides (Li_2S_x) that are produced are highly soluble in the typical liquid organic electrolyte used in Li-ion batteries.

2.3 Li-ion Cell Electrochemical Degradation and Failure Mechanisms

In general, the technical literature indicates that, while there are many factors, the primary parameters controlling Li-ion cell and battery performance are temperature and operating voltage. For each battery chemistry, design, and expected duty cycle, there is a range of temperatures and range of operating voltage in which electrochemistry is dominated by intercalation mechanisms described earlier. Outside this range, undesirable side reactions may occur which can lead to self-heating (exothermic reactions) and/or internal electrical shorts (excessive flow of electrons). This operating window and undesirable side reactions are discussed in more detail in Chapter 7 of this document. Exothermic reactions and/or internal electrical shorts may be triggered by manufacturing defects, or mechanical, electrical, or thermal errors, misuse or abuse (Arora, Medora, Livernois, & Stewart, 2010). If allowed to continue, these reactions or shorts can create conditions for self-heating within the cell; which grow to become uncontrolled increases in temperature and pressure (thermal runaway); and potentially end in venting or catastrophic failure of the cell. Surrounding cells may be affected by elevated temperature and pressure, and cell failure, with the potential for propagation beyond the individual cell. Internal fail-safes to protect against thermal runaway, including electrical controls, physical vents, thermal barriers, and reaction inhibitors, can be designed into the battery cell or pack to limit or prevent the effect of the external abuse on internal heating of the battery; likewise, external cooling systems are being developed to dissipate heat such that internal self-heating reaction temperatures and heating rates are managed.

Any individual or combination of the following types of errors or abuse may initiate failure of a Li-ion cell (Arora, Medora, Livernois, & Stewart, 2010; Balakrishnan, Ramesh, & Kumar, 2006; Bandhauer, Garimella, & Fuller, 2011; Wang, Sun, Yao, & Chen, 2006; Spotnitz & Franklin, 2003):

- Cell overcharge or discharge
- Recharging at low temperatures
- Storing or operating the battery at high temperatures .
- Internal short circuit
- External mechanical abuse
- External short circuit
- Electrochemical aging
- Internal mechanical stress

Any of these “root causes” can initiate or grow damage primarily by increasing a.) interfacial kinetics; b.) chemical species transport; or c.) Joule heating to rates outside of their operational

range with the potential to create conditions for thermal runaway within a cell (Bandhauer, Garimella, & Fuller, 2011). The objectives of several studies on Li-ion battery failure have been to identify how these failure causes occur in individual cells or packs of cells and determine the associated sequence of events (i.e., chemical reactions, temperatures, and rates) that can lead to thermal runaway (Balakrishnan, Ramesh, & Kumar, 2006; Bandhauer, Garimella, & Fuller, 2011; Wang, Sun, Yao, & Chen, 2006; Spotnitz & Franklin, 2003). Knowledge of these failure modes has led to the development of subsystems, devices, and other fail-safes designed to prevent thermal runaway from occurring within the cells as a result of the external stimuli.

Thermal and electrical causes of failure are often coupled together because an increase in one effect (i.e., power surge) typically results in an increase of the other (i.e., local heating). Overcharging or over-discharging cells; short circuiting across cell terminals; storage or operation of the cell in extreme hot temperatures (i.e., above 50°C, [Arora, Medora, Livernois, & Stewart, 2010]); and incompatibilities with the capacitance of cells connected in series are failure causes that have been the subject of several studies (Bandhauer, Garimella, & Fuller, 2011; Arora, Medora, Livernois, & Stewart, 2010).

Following is additional background information on each of these potential root causes of Li-ion cell failure.

2.3.1 Cell Overcharge and Overdischarge

As discussed in detail within Chapter 7 of this report, charging or discharging outside the acceptable range for a particular cell chemistry causes potentially damaging side reactions, excessive current and overheating.

2.3.1.1 Cell Overcharge

As a general rule, cells should not be overcharged. When a cell is allowed to enter into an overcharged state, one of several exothermic reactions has the potential to initiate a thermal runaway process. The effects of overcharge depend on the cathode active material.

In one of these reactions, as a cell overcharges, Li-ions that constitute the physical makeup of the cathode are transferred from the cathode to the anode and accumulate on the anode. If this transfer process continues beyond the normal termination point, so much of the lithium from the cathode material will be removed that it will become chemically unstable. In cells with alkyl carbonate-based electrolytes, delithiated cathode material has been shown to react exothermically with the electrolyte solvent (Balakrishnan, Ramesh, & Kumar, 2006).

Another exothermic reaction caused by overcharging is an increase in the resistance of the active material in the cathode. This happens concurrently with a decomposition of the electrolyte, which will coat the cathode and anode, adding to the increase in resistance. As the resistance continues to rise and the cell continues to be overcharged, heat is generated while electrons continue to flow into the cell.

Additives to the electrolyte can contribute to overcharge protection. Additives that decompose at a cell voltage slightly above the normal operating voltage of the cell can be added to the electrolyte. If any overcharging occurs, the additive exothermically decomposes, which causes pressure build-up. The additional pressure trips a mechanically activated internal circuit breaker known as a charge interrupt device, CID, that disrupts the flow of charge.

Overcharging can also cause plating of lithium onto the anode, often in the form of metallic dendrites that can lead to short circuiting. These side reactions are governed by the electrode overvoltage and the local species concentrations. Generally, conservative limits are set on the cell voltage and current to keep these electrode overvoltages and species concentrations within acceptable ranges.

As described in detail in Chapters 4 and 6, electronic controls can be used to prevent overcharging. In general, if the voltage of a cell exceeds a voltage limit, the control system opens a switch to discontinue the charge. In the instance of an assembly of cells, the control system will balance the voltage of the different cells to keep them all within acceptable limits. If one cell exceeds a limit, the charging for that cell will be discontinued, and the balancing electronics will return the cell to the voltage of the other cells.

2.3.1.2 Cell Over-Discharge

Some Li-ion cells must not be fully discharged. When a deep discharge occurs, the copper material in the anode can oxidize and eventually diffuse into the electrolyte solution. When the cell is recharged, the dissolved copper can re-plate back onto the anode. After many cycles of complete discharge, metallic dendrites can grow between the electrodes and through the separator to create an internal short circuit.

2.3.2 Excessive Temperatures

Temperatures within a cell directly affect the rate of electrochemical reactions, increasing and decreasing with temperature. Cell temperatures may be affected by internal self-heating as well as by ambient temperatures of the array, module, pack and vehicle.

2.3.2.1 Recharging Battery in Low Temperatures

Metallic dendrites can grow when a battery is recharged at a low temperature because some processes within the cell are more affected by the cold than others. During recharging, Li-ions move from the electrolyte layer to the SEI and from the SEI to the anode. When the cell is too cold, Li-ions can be deposited onto the SEI layer faster than they can diffuse from there to the anode. The excess Li-ions plate onto the SEI layer of the anode, forming dendrites and possibly creating an internal short circuit.

2.3.2.2 Storing the Battery at Elevated Temperatures

When a Li-ion battery system or cell is stored in high-temperature environments, there is an increased risk for of failure resulting from breakdown of the protective SEI layer and/or vaporization of the electrolyte. When the SEI layer is compromised in the first mode, typically around 120°C, the anode will exothermically react with the electrolyte solution. In the second breakdown mode, major components of the electrolyte solution are volatile compounds, which vaporize into a gas inside the cell at higher temperatures. This vaporization will increase the pressure inside the cell, which could activate the electronic interrupting devices.

2.3.3 Internal Short Circuit

Internal cell short circuits result in excessive flow of electrons within the cell, increasing Joule heating and increasing temperatures, again potentially contributing to thermal runaway. Several different initiating events or physical entities have been hypothesized to lead to an internal short circuit (adapted from Arora, Medora, Livernois, & Stewart, 2010), including

- Incorrect charging
 - Incorrect charging protocols for the specific battery chemistry
 - Charging occurring at temperatures above the rated temperature
 - Charging at low temperatures, which causes plating
 - Overdischarge leading to copper plating.
- Cell internal component failures
 - Failure of the separator material, particularly related to repeated cycling
 - Shrinkage of the separator allowing edge contact of the electrodes or current collectors
 - Nano-particles detaching from the electrodes
- Undesirable side reactions
 - Lithium plating
 - Growth of dendrites
- Errors in cell design and/or manufacturing
 - Improper design of the cell tabs.
 - Internal cell contaminants
- Mechanical abuse of the cell

Inside a Li-ion cell, four system components may be involved in an internal short circuit. These are the copper current collector on the anode, the anode material, the aluminum current collector on the cathode, and the cathode material. These components can interact with each other in the following combinations to create an internal short circuit between

- The copper current collector and the aluminum current collector
- The copper current collector and the cathode material
- The aluminum current collector and the anode material
- The active material in the anode and the active material in the cathode.

The cell design and assembly processes may introduce several sources of internal short circuits. For example, poor quality control of the assembly process may result in encasing metallic particle contaminants in the cell (Arora, Medora, Livernois, & Stewart, 2010). If a significant amount of these contaminants are present in the cell, short circuits could become a concern. Factors that may contribute to cell defects encountered during the assembly process therefore should be identified, monitored, and avoided.

The existence of metallic particles in the cell also creates the opportunity for other shorting mechanisms. A small number of iron particles that exist as contaminants in the active material during manufacturing of the anode or cathode active material can be converted to a soluble iron during the charge and discharge process when the potential of the electrode in that region is greater than the oxidation potential of iron. The iron ions that become part of the electrolyte solution will diffuse to the opposite electrode from where they initiated. Once at the other electrode, they can be converted back to iron. This back and forth process can lead to the growth of dendrites that puncture the separator and create a shorting circuit between the electrodes.

In addition to material impurities, defects can be introduced to the cell during the manufacturing of the individual components or during their assembly. These defects are typically related to each component's relative positioning to the others within the cell. Assembly misalignments can

include the cell tabs being positioned incorrectly, the cell tabs being installed incorrectly, or portions of the electrodes being crushed due to winding misalignments.

An internal short condition can also be initiated due to incorrect charging. Li-ion cells are typically charged at a constant current until the voltage reaches a set upper limit, and then charging is driven by a constant voltage until the current decreases to a low, set-point value. If continuous low-current charging (trickle charging) is performed at all, the solvents in the electrolyte can become oxidized. This can then result in the degradation of the cathode material and plating of lithium on the anode material, leading to the potential for a short circuit.

2.3.4 External Abuse

External events such as mechanical loadings and electrical short circuits can damage internal components, increasing the likelihood of failure.

2.3.4.1 External Mechanical Abuse

Mechanical abuse can induce precursors to thermal runaway events. Abuse such as dropping, crushing, or puncturing of the cell or pack of cells can produce localized internal heating of the cell as a result of frictional heating from impact, or internal shorting from a) compressing of cell materials such that separated or shielded cell components come into contact with each other, or b) puncture of the cell with a conductive material (Arora, Medora, Livernois, & Stewart, 2010; Spotnitz & Franklin, 2003). Pouch cells may be susceptible to mild mechanical abuse because these cells are not enclosed by sturdy cases (Mikolajczak, Kahn, White, & Long, 2011).

2.3.4.2 External Short Circuit

An instance where the terminals of the cell are bridged with a conductor that has a resistance less than 50 mΩ is how typical test protocols define an external short circuit. In the event that a fully charged multi-cell battery has an external short circuit, high peak currents can be developed within individual cells. An external short circuit can lead to overtemperature and overpressure of a cell, thereby causing cell to vent, releasing the flammable electrolyte, and possibly creating toxic gases, or rupturing the cell.

Failures of Li-ion battery systems have been observed when a short circuit on the cell protection circuit board occurred. This led to a large amount of current being released into the current carrying bus bars, which were not designed to handle peak loads observed with circuitry failures.

2.3.5 Aging and Internal Mechanical Stress

Failures of Li-ion cells encompass both failures that lead to safety issues and failures that limit optimal performance or cycling of the battery versus the design intent and need. Although the primary focus of the discussion here is on failures that lead to safety issues, incidents related to Li-ion cell failure usually take place after the battery has been in use for some time. Therefore, it is critical to identify the correlation between stress and aging effects and the battery behavior to address Li-ion safety issues (Wu & Wang, 2011).

Battery failures that lead to sub-optimal performance can often be traced back to aging mechanisms within the cell. The cathode and the anode age differently, and the majority of aging in the system takes place at the interface of the separator, the electrolyte, and the cathode or anode. Aging at either electrode can lead to a change in its properties that varies with both calendar time and use. During storage, self-discharges and increasing impedance can shorten

shelf life. In addition, trace contaminants, such as water and iron, can have significant effects on the degradation. The cycle life is typically influenced by stress induced degradation and lithium metal plating.

When the anode is in a charged state, electrolyte decomposition products react with an irreversible consumption of Li-ions to form the SEI, which impedes further decomposition. The SEI limits the reaction between the electrolyte and the anode, while still allowing lithium cations to diffuse between the anode and the electrolyte. Once the SEI is formed, it protects against continued reduction of the electrolyte materials and also protects the anode from corroding. However, the capacity of the battery is reduced by the amount of lithium that is incorporated into the SEI.

The diffusion of the lithium into and out of the anode introduces several possible degradation paths. The intercalation of lithium into the anode results in a swelling of the anode, resulting in diffusion induced stress (Deshpande, Verbrugge, Cheng, Wang, & Liu, 2012; Renganathan, Sikha, Santhanagopalan, & White, 2010). The stress can lead to fractures and crack growth, which act to expose fresh anode surface to the electrolyte. This exposed surface then reacts with the electrolyte to form additional SEI material, further decreasing the cell's capacity. The lithium diffusing through the existing SEI layer can also react with the SEI layer to increase its thickness, further contributing to aging and capacity fade (Deshpande, Verbrugge, Cheng, Wang, & Liu, 2012). Some research is also being performed on using alternate coatings on the electrodes to avoid lithium depletion due to SEI formation.

Several studies have explored diffusion induced stress in anodes, with several significant findings. One of the most significant finding is the relation between the charge/discharge rate and the stress, with the stress increasing as the C-rate increases (Fu, Xiao, & Choe, 2013; Grantab & Shenoy, 2011). The stress is also larger at the interface with the separator (Fu, Xiao, & Choe, 2013; Renganathan, Sikha, Santhanagopalan, & White, 2010). The size of the particles also determines the magnitude of the stress, with smaller particles having lower stress (Daniels and Besenhard, 2012). The morphology of the electrode can also act to reduce stress, if the size and morphology of the other electrode components is properly balanced (Bhandakar & Johnson, 2012). The magnitude and orientation of the stress can lead to cracking of the electrode materials (Grantab & Shenoy, 2011), which may lead to increased impedance of the electrodes (Woodford, Carter, & Chiang, 2012).

The diffusion of lithium onto and out of the cathode can also lead to a swelling of the cathode, although the magnitude of the swelling is often less than for the anode (Lee, Lee, & Ahn, 2003). This behavior of the cathode is similar to that of the anode, in that the diffusion induced stress can lead to cracking of the electrode materials. Additional stress can occur in the cathode due to phase transformations of the oxide at high state of charge (Renganathan, Sikha, Santhanagopalan, & White, 2010). The inhomogeneities present in the cathode can also act to increase stress (Shearing et al., 2012).

The swelling of the anode and cathode during charge and discharge can lead to change in dimensions (swelling) of the cell. This change has both a reversible and irreversible component, with the magnitude dependent on the exact cell chemistry. The reversible change in cell thickness depends solely on the SOC of the cell (Fu, Xiao, & Choe, 2013), and can result in an increase in thickness of greater than 2% (Lee, Lee, & Ahn, 2003). The irreversible swelling of the cell is associated with an increase in pressure inside the cell and is caused by the formation of

the SEI. The largest component of this change occurs during the first charge cycle, when the SEI is initially formed, but the swelling continues during the life of the cell. The swelling is often less of an issue for pouch cells, as they can be vented and re-sealed after the first charge cycle (Lee, Lee, & Ahn, 2003). The repeated change in cell pressure can cause any burrs or sharp contaminants to puncture the separator (Mikolajczak, Kahn, White, & Long, 2011).

In addition to compositional changes in the cathode or anode contributing to stress and aging in Li-ion cells, lower operating temperatures also play a role in reduced performance in colder environments. Li-ion chemistries work because Li-ions transfer back and forth and diffuse into layers between the cathode and anode as the cell is cycled. As external environmental temperatures increase or decrease, the transfer of ions is affected and cell performance is less than optimal; therefore, many commercial battery designs include cell temperature controls to prevent performance degradation. Also, depending on the chemistry of the individual components of the cell, a high state or low state of charge over long durations can shorten battery life and lessen performance. The varying starting points for chemistry of the cathode, typically different versions of a lithium metal oxide, alter how a cell ages. This is because each material has variations in particle size, distribution, and surface area. All of these factors influence cell life and breakdown in performance.

2.3.5.1 Other Sources of Internal Mechanical Stress

There are many sources of internal mechanical stress in the Li-ion battery cell, including stress induced during manufacturing from calendaring² the electrodes (Yi, Wang, & Sastry, 2006), stress induced by packaging the cell (Lee, Lee, & Ahn 2003; Wang, Sone, & Kuwajima, 2004), and stress induced by electrochemical cycling as described in the previous section (Zhang, Wang, & Tang, 2012). The mechanical stress can lead to increased surface area of the electrode materials, loss of continuity in the electrodes, and a decrease in the free volume within the electrodes (Daniels and Besenhard, 2012).

Additional stress can arise in the cell due to mismatch in the thermal expansion coefficient between different electrode materials, and differences between the electrode and current collectors. The thermal changes of the cell can arise both from changes in the ambient environment and exothermic reactions or resistive heating within the cell.

It is important to point out that internal mechanical stress effects on durability differ substantially from electro-chemical effects on durability. Battery cells are a multi-physics combination of electro-chemistry, electrical, mechanical, and thermal processes that do not scale equally with any single parameter such as stress.

2.3.6 Damage Mechanics Perspective

The discussions of electrochemically induced and mechanically induced stress in the previous sections are consistent with damage mechanics processes of damage incubation, initiation, and growth at the local electrochemistry level. As discussed above, intercalation of lithium into the anode results in a swelling of the anode and diffusion induced stress. The stress can incubate and initiate fractures and crack growth, which act to expose fresh anode surface to the electrolyte. Repeated stress cycles may cause long-term growth of fractures and cracks until they ultimately

² Calendaring an electrode is the process of running the electrode between a series of rollers to achieve uniform thickness of the Electrode material.

cause internal shorts. The analysis of electrochemical reactions outside the range of normal charge/discharge intercalation mechanisms described in Chapter 7 further supports application of the damage mechanics perspective to Li-ion battery performance. For the purposes of this investigation, damage is defined electrochemical reactions outside the range of normal charge/discharge intercalation mechanisms, such as such as Li plating, copper dissolving, or SEI thermal breakdown, as well as the initiation and formation of fractures and cracks.

Crack growth and electrochemical damage reactions are both time-dependent processes, suggesting that Li-ion cell failure is also a time-dependent process. The time scale may be very brief or very long. While failure can sometimes occur very rapidly after a cell is damaged, damage may also sometimes grow over many years and many duty cycles, causing delayed failure long after damage is initiated.

The concept of damage initiation and growth during subsequent service loadings is well established in mechanical systems design, but appears to be in its early stages of understanding in Li-ion battery literature. The concept of damage is leveraged here from experience with other high-energy storage systems such as hydrogen fuel tanks, which may be damaged by impacts from dropping or excessive temperature, both of which are events that can also damage Li-ion batteries and their components.

Damage initiation and long-term growth to failure are important concepts for performance-based assessment and testing of Li-ion battery safety. In addition to abuse event test cases that cause rapid failure, cells and batteries must be subjected to duty cycles wherein damage may be induced by service extremes, followed by charge/discharge cycles that can grow that damage to failure. This concept is discussed in more detail in Chapter 9.

2.4 Cell Electrochemical Failure Mitigation Methods

Cell component-level mitigation methods include strategies to detect conditions that could lead to thermal runaway; activate fail-safes that essentially shut down the chemical processes associated with thermal runaway; and integrate alternative component materials into the cell design that could preclude and prevent unwanted internal exothermic reactions associated with some of the existing component materials.

In some instances, battery electronics can be used to prevent thermal runaway. Li-ion batteries typically contain several thermo-electrical components, safety vents, and fuses to detect and prevent possible failure. These devices are typically used to prevent cell external short circuit, cell overcharge or overdischarge, or other abuse conditions. More information on this topic is provided in subsequent chapters.

Many cell designs contain a polyolefin, polyethylene, or polypropylene microporous separator between the cathode and anode (NAVSEA, 2009). Under normal operating conditions, the separator controls the flow of all ionic process between the electrodes. However, during elevating temperatures and heating rates indicative of possible thermal runaway, the separator will shut down, effectively closing the pores and preventing inter-electrode chemical reactions to occur (Balakrishnan, Ramesh, & Kumar, 2006). Upon shutdown, the internal temperature within the cell may either drop back down to safer levels, or continue to rise due to significant thermal inertia or internal short-circuit across the closed separator (Balakrishnan, Ramesh, & Kumar, 2006). If the latter occurs, the separator may eventually reach the point of no return known as “separator breakdown” (Balakrishnan, Ramesh, & Kumar, 2006; Arora, Medora, Livernois, &

Stewart, 2010). At the point of breakdown, the separator melts and the probability of internal short circuit and thermal runaway increases (Arora, Medora, Livernois, & Stewart, 2010). As the temperature reaches 175 to 185°C, the polypropylene component of the separator can melt, which can, in turn, increase the probability of the initiation of an internal short circuit (Arora, Medora, Livernois, & Stewart, 2010).

There is significant research examining alternative materials that further reduce the risk of thermal runaway. One solution has been to develop cathode materials that are less sensitive to overcharge, or that have much higher thermal stability than standard cathode oxides. Another possible solution to thermal runaway initiated from SEI breakdown and Li-ion reaction with the electrolyte would be to use an alternative anode active material such as lithium titanate, which operates at a voltage range where SEI formation is minimized.

New developments in ceramic separator materials are being investigated to create a barrier between the cathode and anode that does not melt during the initial exothermic reaction phases.

The effect of heating the organic solvent within the electrolyte has also received considerable attention. Recent efforts have been made to integrate the use of flame retardant chemicals, such as fluorinated and organophosphorus-based additives, to the organic solvent to inhibit combustion, effectively preventing or suppressing combustion reactions between fuels and oxygen (Balakrishnan, Ramesh, & Kumar, 2006). Ionic liquid-based electrolytes, which exhibit low volatility, high thermal stability, and adequate ionic conductivity, are also being developed as a possible replacement or additive to the more flammable organic solvents (Arbizzani, Gabrielli, & Mastragostino, 2011). These material alternatives have been discussed in greater detail in previous sections.

2.5 *Electrochemistry of Cell Thermal Runaway*

The irreversible electrochemical reactions that occur during damage and failure are exothermic and may generate gases, resulting in the buildup of excess heat and excess pressure within a cell. Additionally, the irreversible reactions are accelerated by increasing temperature from excess heat, with the potential for thermal runaway. Compression of the electrochemical component layers in a cell due to diffusion of lithium into and out of anodes and/or external mechanical forces can also accelerate electrochemical reactions, contributing to damage and failure propagation. Cells are tightly packed together for performance and packaging reasons. Consequently, excess heating and mechanical pressure from a failing cell can induce damage and potential failure of adjacent cells. If not mitigated by safety systems, failure can propagate, uncontrolled, from cell-to-cell, potentially achieving a catastrophic failure of an array, module, and battery system.

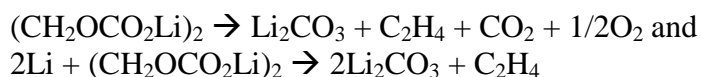
Thermal runaway is most likely to be realized when an event occurs that results in rapid heating of the cell that outpaces the rate of heat dissipation in the cell (Mikolajczak, Kahn, White, & Long, 2011). Cell heating can be caused by thermal (e.g., radiant heating), electrical (e.g., short circuiting), or physical (e.g., compression) external effects. The key parameters to controlling thermal runaway are limiting the rate of heat generation and ensuring that the rate of heat removal exceeds the rate of heat generation. However, even if the charging/discharging and thermal management controls are functioning properly, the rate of heat generation could be such that the controls cannot react quickly or adequately enough to dissipate the heat (Balakrishnan,

Ramesh, & Kumar, 2006). Consequently, passive thermal dissipation of local heating is an active field of battery thermal management (Kim et al., 2010).

The following sequence of reactions is thought to take place during most thermal runaways in Li-ion batteries; note that not all of these events must occur or occur sequentially. The types of reactions and temperatures at which they occur are discussed in general terms. Several studies, as cited below, report various temperature ranges at which these events occur. The following series of events represents a hypothetical chain reaction in a cell that has a lithium cobalt cathode. Figure 2-5 provides a graphic illustration of the temperature ranges for each of these events.

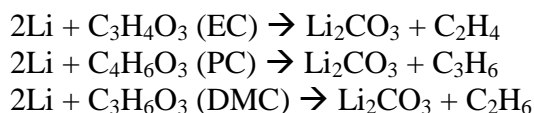
SEI Layer Decomposition: Upon initial charging, the Li-ion cell will develop the SEI layer at the anode. The SEI layer formation provides a loss in the capacity of the cell. The SEI layer begins to decompose once temperatures reach approximately 85 to 90°C, with decomposition continuing up to approximately 120°C (Bandhauer, Garimella, & Fuller, 2011; Spotnitz & Franklin, 2003; Wang, Sun, Yao, & Chen, 2006). Temperatures as low as approximately 60 to 80°C have also been reported for the onset of SEI layer decomposition in a Li-ion cell with a lithiated cobalt oxide positive electrode (Arora, Medora, Livernois, & Stewart, 2010).

The SEI contains stable (e.g., LiF and Li₂CO₃) and metastable (e.g., (CH₂OCO₂Li)₂) components (Spotnitz & Franklin, 2003, Wang, Sun, Yao, & Chen, 2006). During SEI decomposition, the metastable component could decompose exothermically, producing flammable gases (ethylene, C₂H₄) and oxygen via:



Reaction of Intercalated Lithium with Electrolyte: Decomposition of the SEI exposes intercalated lithium of the negative electrode, which can rapidly react with the electrolyte organic solvent at temperatures starting at 125°C and peaking at 218°C. During this rise in temperature, a secondary SEI layer can be formed and successively decomposed via reactions identical to those given for the initial SEI layer decomposition, with a peak at temperature of approximately 230°C (Wang, Sun, Yao, & Chen, 2006; Bandhauer, Garimella, & Fuller, 2011), releasing more heat with decomposition.

Further Reaction of Intercalated Lithium with Electrolyte: Once the secondary SEI layer breaks down, the intercalated lithium of the negative electrode reacts again with the electrolyte to form lithium carbonate and additional flammable hydrocarbons (ethylene; ethane, C₂H₆; and propylene, C₃H₆). These reactions occur at temperatures above 200°C, with a peak temperature of approximately 250°C and include:



Electrolyte Decomposition: As the temperature within the cell increases above 200°C, electrolytes can decompose exothermically (Spotnitz & Franklin, 2003). For example, EC can decompose to carbon dioxide and ethylene oxide; ethylene oxide can then also decompose exothermically. Specific data on the tendency of electrolytes to decompose and the resulting severity has been noted to be somewhat contradictory and imprecise (Spotnitz & Franklin, 2003).

Reaction of Intercalated Lithium with Binder: Starting at temperatures of 220°C, the lithium present in the negative electrode can start to react exothermically with fluorinated binders

(Spotnitz & Franklin, 2003), although reactions between the negative electrode and electrolyte may occur first and deplete the available lithium (Bandhauer, Garimella, & Fuller, 2011). These reactions may include:

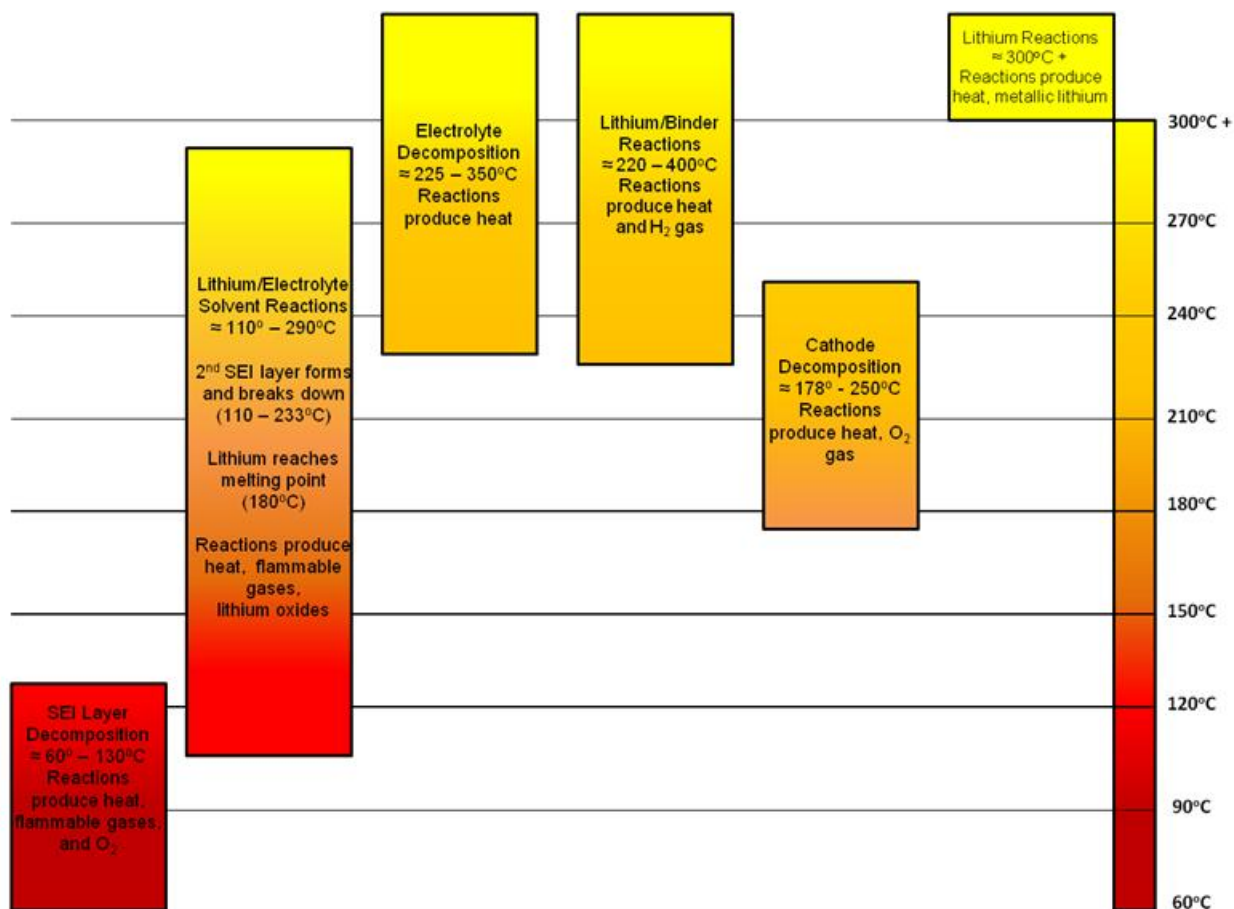
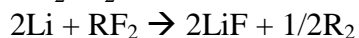
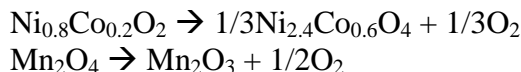
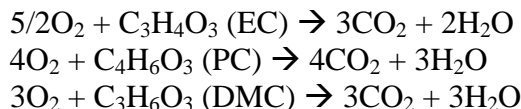


Figure 2-5. Illustration of possible temperature ranges for chemical breakdown of Li-ion cell components in an example thermal runaway event.

Positive Active Material Decomposition (and possible electrolyte combustion): When temperatures reach the range of 178 to 250°C, positive active material decomposition and cathode/electrolyte reactions occur. This cathode/electrolyte reaction is exacerbated at over-voltages and with excessive de-lithiation of the cathode (from overcharging). The cathode can decompose exothermically, releasing oxygen:



The oxygen liberated from these reactions can, in turn, react with the electrolyte solvent. Combustion reactions such as:



can occur if worst-case conditions are satisfied within the cell i.e., the availability of the solvent and oxygen—and the temperature—are such that a flame develops (Spotnitz & Franklin, 2003; Bandhauer, Garimella, & Fuller, 2011).

Lithium Reactions: At extremely high temperatures (greater than 300°C), metallic lithium can form from the decomposition of LiF and Li₂CO₃, and the graphite portion of the anode can exothermically decompose. However, not much data is available on the frequency or characteristics of these reactions (Spotnitz & Franklin, 2003).

Cell Venting and Rupture: If heat generation is allowed to outpace the rate of heat dissipation (thermal runaway), pressure could rise within a cell sufficient to open its pressure venting device, or possibly rupture the cell. As described in the next chapter, many cell designs include pressure relief devices that open in the case of overpressure to prevent excessive expansion of the cell casing and, potentially, casing rupture. Rupture is possible in the case of heat induced overpressure if pressure venting is not included in the cell design, if heat generation outpaces the vent response time, or if a pressure venting component fails or is defeated by other means. In such cases, the pressure at which rupture occurs and the nature of the rupture is dependent on the strength of the casing material at elevated temperatures.

The severity of the post-venting or post-rupture reactions will depend on the chemical state of the cell at the moment of rupture. If organic electrolyte solvent is ejected from the battery during venting or rupture, contact with nearby ignition sources (sparks or hot surfaces) can result in fuel vapor fire (“fireballs”) that may pose a significant threat to persons near the ruptured cell. Other vented materials may include additional combustible gases such as hydrogen (H₂) and carbon monoxide (CO) and toxic or corrosive materials, such as hydrofluoric (HF) acid.

Similar arguments can be made concerning the potential for venting and/or rupture at the array, module, and pack level. Heat generation greater than heat dissipation (thermal runaway) of multiple cells can cause the pressure to rise within any sealed subsystem sufficient to open pressure venting devices, or possibly rupture the subsystem.

2.6 Electrolytic Solvent Combustion Properties

If pressure within a cell rises sufficiently to open a pressure venting device, or possibly rupture the cell, there is potential for venting of combustible electrolytic solvent materials. Threat analysis should consider properties of the combustible electrolytic solvent materials such as the following: vapor pressure, autoignition temperature, flash point, upper and lower flammability limit, stoichiometric range, minimum oxygen concentration, and minimum ignition energy. Knowledge and understanding of these properties can help alleviate the threats and consequence posed by cell rupture and dispersion of hazardous materials. Additionally, preventing the ruptured, combustible material from coming into contact with ignition sources, including hot surfaces, electrical sparks, or mechanical sparks, is imperative to the secondary threat safety analysis.

Shown in Table 2-8 are the most common electrolytic solvents used in Li-ion batteries, which are flammable.³ This property is intended to mean that, in addition to the primary effects from the failure mode of thermal runaway, notably cell or container breaching or bursting resulting from the softening of materials and from elevated pressures, there can be secondary effects, predominantly fire and explosion, resulting from the high-temperature chemical combustion reactions initiated by the thermal runaway.

Table 2-8 was prepared to: (1) characterize the propensity and severity of the fires that could result from thermal runaway initiating combustion of a flammable electrolytic solvent; and (2) compare the propensity and severity of these flammable materials with those used in conventional and alternative vehicular fuels, namely gasoline, diesel, natural gas, propane, and hydrogen. Critical characteristics assessed included: vapor density, flash point, lower and upper flammability limits, minimum ignition energy, auto-ignition and maximum (adiabatic) flame temperature, maximum blast overpressure, and energy value. Data for these characteristics were taken from published technical sources, which are typically reported on a chemical's material safety data sheet.

³ The term "flammable" has more than one meaning and the intent can be misconstrued. The formal scientific definition of flammable liquid is having closed cup flash points below 100°F (37°C) and vapor pressures not exceeding 40 psi (276 kPa) (2.76 bar) at 100°F (37°C). Flammable liquids are referred to as Class I liquids. Combustible liquids are defined as liquids having closed cup flash points at or above 100°F (37°C). Combustible liquids are referred to as Class II or Class III liquids.

Table 2-8. Comparative propensity and severity of fires from flammable vehicular fuels or Li-ion battery solvents.

Flammable Gas or Liquid	Vapor Density	Flash Point	Flammability Limit		Auto-Ignition Temperature	Minimum Spark Energy	Adiabatic Flame Temperature	Maximum Blast Overpressure	Energy Value
	Air =1	°C	Lower	Upper	°C	mJ	°C	atm	MJ/L
			%	%					
Vehicular Fuel									
Hydrogen	0.07	Gas	4	75	520	0.002	2072	7.9	2
Gasoline	2 to 4	-40	1.4	7.6	300	0.045	1998	7.8	33
Diesel	4 to 6	52	0.6	5.6	230	0.070	2002	7.8	37
Natural Gas	0.6	Gas	5	15	630	0.025	1927	7.5	9
Propane	1.5	Gas	2	9	450	0.025	1967	7.6	24
Li-Electrolytic Solvent									
Diethyl Carbonate	4.0	25	Flammable	Flammable	445	~≥0.025	~2000	~7.8	21
Dimethyl Carbonate	3.1	18	4.2	12.8	UNK	~≥0.025	~2000	~7.8	16
Ethylene Carbonate	3.0	143	3.6	16.1	465	~≥0.025	~2000	~7.8	17
Propylene Carbonate	3.5	132	Flammable	Flammable	510	~≥0.025	~2000	~7.8	20

The following observations can be made from Table 2-8.

- Upon release, flammable electrolyte solvents in Li-ion batteries would not leak as liquids due to the cell construction but would disperse as vapors much heavier than air, behaving similarly to gasoline and diesel fuels, which would tend to remain beneath the vehicle or battery and not readily disperse, localizing the fire to that vicinity and increasing exposure of occupants to fire.
- Flash points of some of the more prevalent electrolytic solvents, diethyl and dimethyl carbonate, are “low” and somewhat comparable to those of gasoline and diesel, whereas those for ethylene and propylene carbonate are much higher than those for vehicular fuels, meaning that higher ambient temperatures would have to be achieved for sufficient vapor (flash point) to be present for ignition. Because the lower the flash point, the more hazardous the fire risk, flammable electrolyte solvents in Li-ion batteries are more or less as hazardous as conventional vehicular fuels.
- The flammability ranges of electrolytic solvents are comparable to those of natural gas and propane; not much wider than those for gasoline and diesel; and much narrower than those for hydrogen. Because the narrower the flammability range, the less hazardous the fire risk, flammable electrolytic solvents in Li-ion batteries are about as hazardous as conventional vehicular fuels, and certainly less hazardous than hydrogen.
- The minimum ignition temperatures for the flammable solvents are comparable to those of natural gas, propane, and hydrogen, and much higher than gasoline and diesel fuels. Because the lower the minimum ignition temperature, the more hazardous the fire risk, flammable electrolytic solvents are not as hazardous as conventional vehicular fuels.
- The minimum ignition (spark) energies for common Li-ion organic solvents appear to be unknown, a significant data gap given that inadvertent spark discharge could be a likely mode of ignition. Based on chemical makeup and data on hydrocarbon flammability, electrolytic solvents are estimated to have minimum ignition energies comparable to gaseous and liquid vehicular fuels. Because the lower the minimum spark energy, the more hazardous the fire risk, flammable electrolytic solvents are probably about as hazardous as conventional vehicular fuels.
- Although not reported, estimated adiabatic (maximum) flame temperatures for the hydrocarbon-based electrolytic solvents are probably comparable to those of the other flammable hydrocarbons. Because the lower the maximum flame temperature the lower the exposure risk (skin burns) to fire, electrolytic solvents are expected to pose no more of a severe risk to burn injuries than conventional vehicular fuels, gasoline and diesel.
- Because of the probable similarity in the magnitude of the maximum flame temperatures, if the combustion of the electrolytic solvents were confined, the resulting overpressure that could build up would maximize at about the same levels as for the other flammable fuels, meaning that the burst damage that would result from Li-ion explosions would also be comparable to that from conventional vehicular fuels.
- The thermal energy expected to be released upon initiation and combustion of the electrolytic solvents would be less than that of gasoline and diesel fuel.

These data were then used to answer the general question

All factors being equal (which they are not), how would these flammable liquids and gases compare in terms of an overall order of propensity and severity?

with the observation

The propensity and severity of fires and explosions from the accidental ignition of flammable electrolytic solvents used in Li-ion battery systems are anticipated to be somewhat comparable to or perhaps slightly less than those for gasoline or diesel vehicular fuels, with the overall consequences for Li-ion batteries also expected to be less because of the much lower amounts of flammable solvent released and burning.

A similar conclusion was reached in a recent study, which concluded that flames of carbonate solvents were generally less energetic than those of conventional hydrocarbons, with flames burning from dimethyl carbonate having only half the peak heat release rate of an analogous propane flame (Harris, Timmons, & Pitz, 2009).

The often touted “solution” to this fire-safety problem would be to use non-flammable solvents. One challenge, however, is that there is an inverse relationship an electrolyte’s performance in a cell and its flammability. Because battery performance cannot be sacrificed, studies have focused on electrolytes with “low,” “less,” or “not easy” flammability within at least the same electrochemical window.

2.7 Summary

Li-ion batteries contain or can produce, via decomposition reactions initiated by failure mechanisms, chemicals that can pose significant flammability, asphyxiation, material compatibility, or toxicity hazards to vehicle passengers and first responders. These hazardous conditions could be realized when the integrity of a battery casing is compromised, causing the release of volatile, flammable, and toxic chemicals from the battery.

A complete assessment of the potential hazards associated with internal or external failure of a Li-ion battery should take into account the amount of material present in a battery and the severity of the hazardous event: e.g., if more than one battery undergoes thermal runaway or is compromised. Knowledge of the specific chemicals present in the battery and the byproducts associated with their decomposition or other thermally induced reactions is necessary for identifying the threat posed by a compromised battery to vehicle passengers and first responders.

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3 Li-ion Cell Design and Safety Performance

As described earlier, the fundamental building block of any battery is the cell. Cells package the cathode, anode, current collectors, electrolyte, and separator components into a practical functional subsystem that stores energy in electrochemical form. Cells provide electrical poles to support electrical charge and discharge. Cells provide mechanical and environmental protection for the components. Cells can also incorporate safety features intended to prevent or mitigate serious failures. Cell electrochemistry defines the fundamental voltage, and design and construction determine the energy storage capacity. As the fundamental building blocks, multiple cells can be assembled in modules to deliver the required voltage capacity required for an application. And modules can be further assembled into battery packs and systems to supply the necessary energy. Alternatively, cells can be assembled directly into battery packs.

This chapter describes the design and construction of Li-ion battery cells, focusing on their electrical, thermal, mechanical, and safety characteristics.

3.1 *Cell Design and Construction*

Li-ion cells in vehicle batteries come in a variety of shapes or types. These cell types are known as cylindrical, prismatic, elliptical, pouch, and large format. All cells relevant to this discussion have liquid electrolyte. Some battery pack manufacturers build upon cylindrical cells because of their high reliability and prevalence in the market. Other manufacturers favor the prismatic type because of its potential for larger power and energy densities and geometrical conformity to the overall pack design. Elliptical cells are similar to prismatic cells in construction, and pouch cells are generally a type of Li-ion polymer that may use a combination of dry and gel electrolyte. Other variants of these cell types may be present or emerging in the market.

3.1.1 Cylindrical Cells

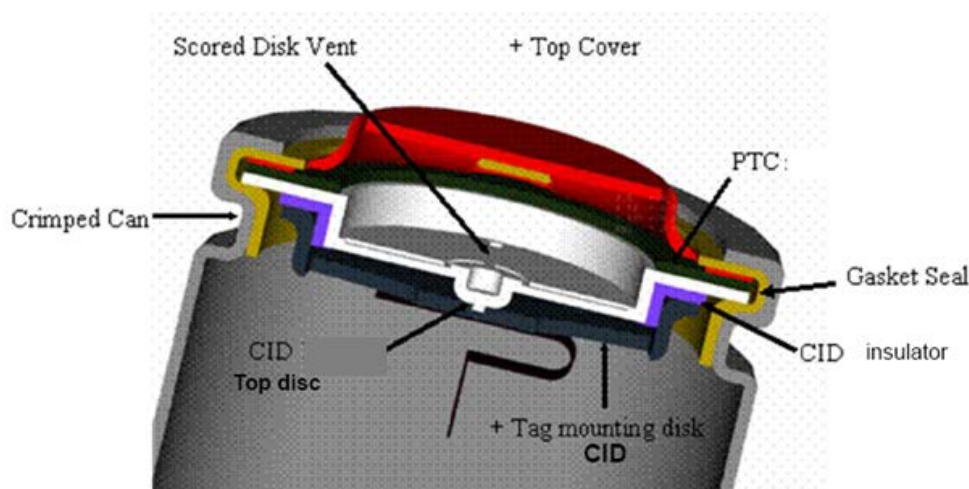
Cylindrical cells have the familiar cylindrical shape and have long been used as single cells in electronic devices such as cameras and in small series and parallel configurations in other electronic devices such as laptops. Most cylindrical cells have the same basic design, which is depicted in Figure 3-1 (Panasonic, n.a.). Cylindrical cells come in a variety of sizes and are typically defined by their dimensions. For example, a model number 18650 specifies a diameter of 18 mm and a length of 65 mm.



Source: Panasonic, n.a... Reprinted with permission.

Figure 3-1. Images of a Panasonic 18650 cylindrical Li-ion battery cell.

Some of the items listed in Figure 3-1 are fundamental battery components while others are there for protection. The electrolyte, separator, anode, and cathode are necessary for the chemistry to work properly and are discussed in more detail in Chapter 2. The positive and negative poles, the insulator, and the gasket are required for electrical connectivity and sealing. The positive temperature coefficient device, current interrupt device, and exhaust or vent disk are safety features that are designed into the cell package. A more detailed drawing of these protection devices is shown in Figure 3-2. While these figures show the typical components inside a cylindrical cell, other protection features and proprietary designs exist.

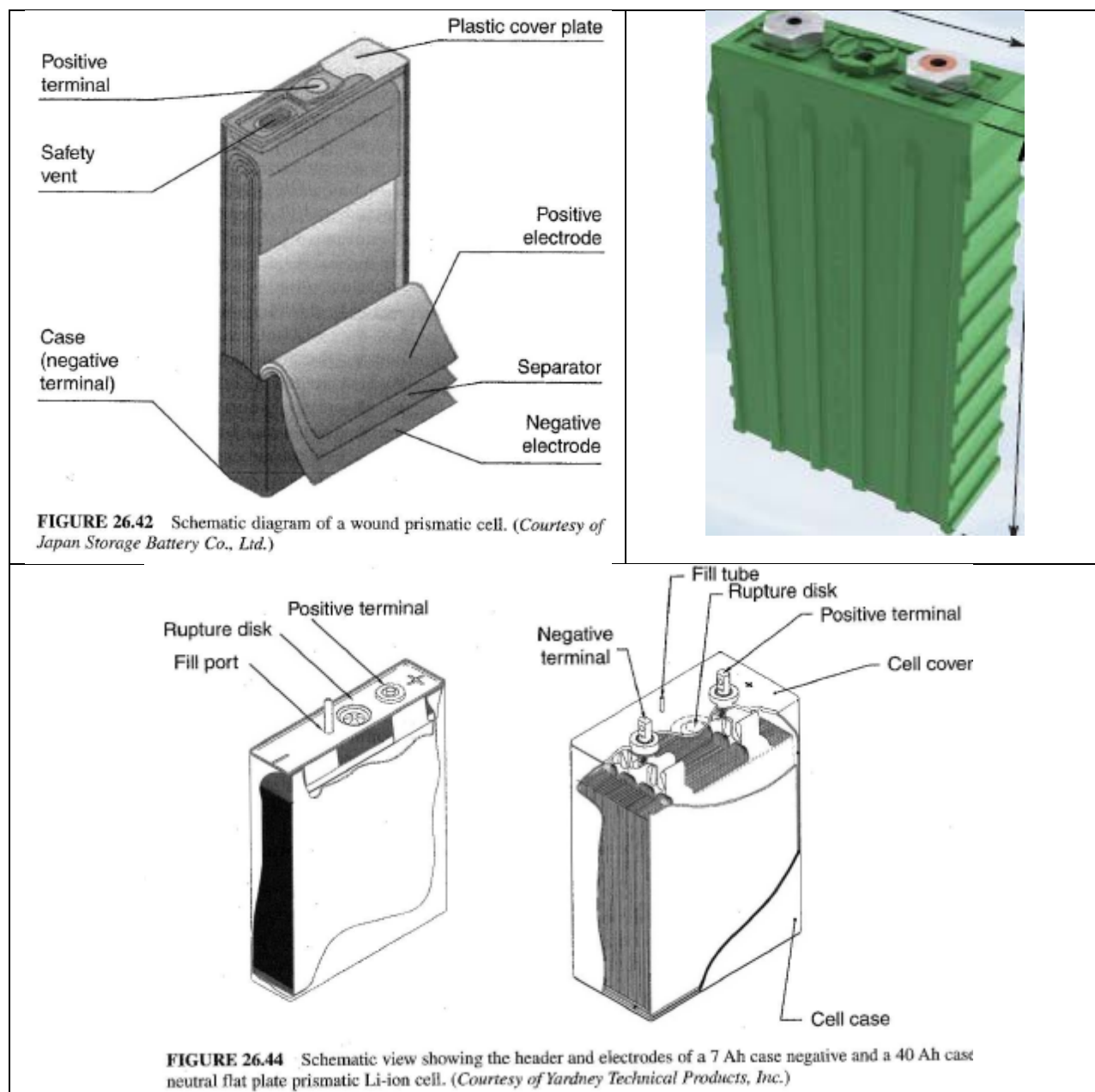


Source: Jeevarajan, 2010. Reprinted with permission.

Figure 3-2. Cutaway drawing of a standard commercial 18650 Li-ion cell.

3.1.2 Prismatic Cells

Prismatic cells are constructed in a wound or flat plate configuration. The difference lies in the manufacturing process. Wound prismatic cells are generally constructed by wrapping the layers around a bobbin or mandrel, similar to that of a cylindrical cell. In a flat plate cell, discrete layers are stacked side by side and pressed together or folded. The folded design is similar to that of a stacked cell except the layers are attached in one large sheet and are folded back over one another and pressed together to form the cell. The layers are contained in a rigid case that provides terminal connections and generally has a vent plug. Similar to cylindrical cells, prismatic cells are generally defined by their dimension where the first two digits refer to the thickness, the next two or three digits represent the width, and the remaining digits represent the length of the cell. Example prismatic cell types are shown in Figure 3-3. The same basic components of cylindrical cells are used to construct prismatic Li-ion cells; however, prismatic cells designed for automotive applications can have much larger capacities than cylindrical cells. So called “large format cells,” discussed in Section 3.1.4, are a form of prismatic cells. If a cell is large (greater than about 10 Ah) the conditions, such as temperature and SOC, are not uniform within the cell during charging or discharging. This increased capacity of these large format cells requires the protective devices to be designed and scaled accordingly. Therefore, some protective devices that work well for smaller cylindrical cells may not be practical or effective for large prismatic cells.



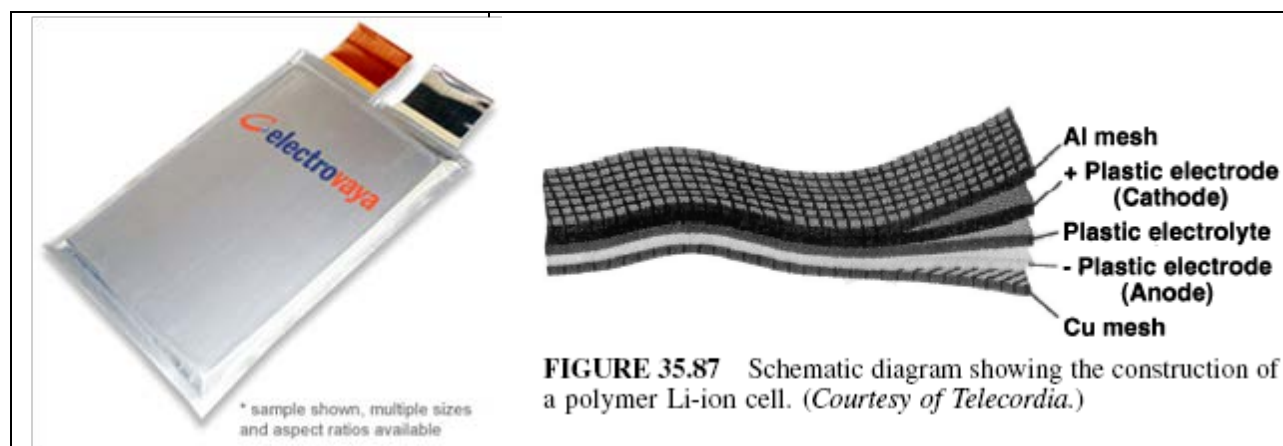
Sources: Reddy & Linden, 2011. Bren-Tronics, 2013. Reprinted with permission.

Figure 3-3. Images of wound and flat plate prismatic Li-ion cells which are also “large format.”

3.1.3 Pouch Cells

Pouch cells are fundamentally prismatic cells with flexible polymer coated aluminum packaging instead of a metal can. The concept originated with the Bellcore “polymer” cell where the electrodes were laminated together with the “polymer” separator. Today numerous cells are made with standard separators and still considered pouch cells. The individual layers are stacked or folded, packed under vacuum and held together by the pouch. If overcharged, the pouch cell releases gases and the pouch may expand, causing the layers to separate. Some manufacturers claim this can be used as a safety feature because the separation of layers causes the cell to stop

working. However, when the cells are packed together into a battery, there may not be sufficient free space for the cell to balloon in practice. In automotive applications, the pouch material offers little physical protection, so the module or battery housing must provide an external structure to support, restrain, and protect the pouch cell. Figure 3-4 shows a typical pouch cell manufactured by Electrovaya as well as an example of the layering (Electrovaya, 2011; NAVSEA, 2009).



Sources: Electrovaya (2011). Reprinted with permission.

Figure 3-4. Picture of an Electrovaya pouch cell and a typical material stackup for a polymer cell.

The tabs or conductors of a pouch cell are typically attached in either an axial or radial fashion. Axial placement allows the tabs to be wider, which, for a given material thickness, lowers total series resistance and increases the ability to conduct heat from the package. The images in Figure 3-5 show examples of these two designs (EnerDel, 2011; LGCPI, 2011).



Sources: EnerDel, 2011. Reprinted with permission.

Figure 3-5. Pictures of two pouch Li-ion polymer cell types, axial electrode configuration (left) and radial electrode configuration (right).

3.1.4 Large Format Cells

Historically, a number of small Li-ion cells have been combined in series and in parallel groupings to produce a battery pack with voltage, current, and storage capacity sufficient to power a motor vehicle. Chapter 4 describes a hypothetical construction of such a pack. An

alternative approach is to build a single, large cell. A large cell has fewer parts than a pack of equivalent capacity that consists of many smaller cells. The smaller parts count offers advantages of ease of assembly, fewer points of failure, and simpler monitoring systems.

“Large format” or simply “large” cells are set apart more by the unique conditions they pose than by a definition threshold or means of construction. A cell of such size that its temperature or state of charge may vary internally, and cannot be assumed uniform, is generally considered to be large format. Technical authors typically identify cells greater than 10 Ah as large. However, as Mikolajczak, Kahn, White, and Long (2011) observe, the term is loosely applied, and in trade literature it may mean a large cell or a high-capacity pack consisting of many smaller cells. The definition of large cells is also linked to transport regulatory requirements that have been subject to change. Based on recent U.N. Model Regulations, a large format cell contains more than 20 hr of energy (e.g., more than 5 Ah capacity with a 3.7 nominal voltage), while a large format battery pack contains more than 100 Wh of energy (e.g., a battery pack containing more than twelve 2.2 hr cells).” (Mikolajczak, Kahn, White, & Long, 2011). Chapter 8 notes that the U.N. Transport Manual has specific definitions and test procedures for “large cell” and “large battery.”

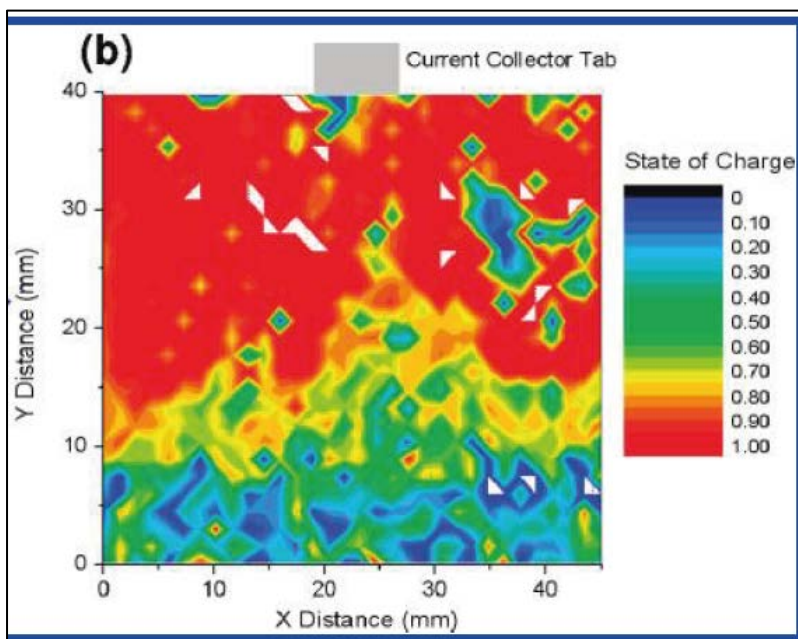
Figure 3-3 above is a photograph of a typical large format cell. As illustrated in the figure, the cell’s internal construction may be similar to the pouch cell in Figure 3-4, but the length of the pouch in a large cell is considerably greater, and the pouch is folded or wrapped around itself to fit the prismatic form of Figure 3-3. A common chemistry in large cells is LiFePO_4 (lithium iron phosphate or LFP), discussed in Section 2.2.

An important consideration in the design of large cells is that internal conditions cannot be assumed uniform as they are in a small cell. Because of their significant separator area, conditions can vary within a large format cell, particularly during charging or discharging. The current distribution within a cell has been shown to be nonuniform during charging and to change as the charging cycle progresses. Similarly as a large cell discharges, the SOC can vary from one point in the cell to another (Zhang, Shaffer, Wang, & Rahn, 2013). This heterogeneity can cause one portion within the cell to be outside the bounds of proper operation while other parts are satisfactory.

Most notably, a single measurement at the terminals may provide information about the average state of charge in a large format cell, but the actual state of charge at different locations within the cell may be well above or below the average. Similarly, the temperature can vary appreciably from one location to another. Intra-cell variations are not measured during operation; they must be inferred from models and experiments. Special behavior and performance models have been developed for large format cells. These variations impose special requirements on the control system and are the subject of ongoing research. Whereas the control system for a pack consisting of many small cells requires complexity to account for possible cell-to-cell variations, the control system for a large cell must account for variations within the cell.

Lee, Kim, and Smith (2010) developed a thermal and electrophysical model of a spirally wound large format cell for automotive applications. They used the model to calculate the optimum number of tabs to achieve uniformity in the cell. In other research, Liu, Kunz, Chen, Tamura, and Richardson (2010) measured the SOC distribution in a 40 x 45 mm rectangular LiFePO_4 pouch and found that the SOC can be above 90% in the half of the cell near the tab and below 60% away from the tab, as illustrated in Figure 3-6. Zhang, Shaffer, Wang, and Rahn (2013) have measured the distribution of SOC during the discharge of a large cell. Section 7.4 summarizes

the efforts of other researchers to model the distribution of charge, temperature, and mechanical stress in cells, including large cells.



Source: Liu, Kunz, Chen, Tamura, & Richardson.

Figure 3-6. Measurement of SOC distribution in a rectangular pouch cell.

Orendorff (2012a) explains the special requirements of a separator in a large format cell and is working to develop a separator better suited to large cells (Orendorff et al., 2012b).

3.2 Design Considerations

As noted throughout this report, thermal runaway of a Li-ion cell is one of the fundamental failure mechanisms leading to safety hazards from Li-ion batteries. Cell heating is normal, but temperatures must be maintained within a predetermined safe operating level. Thermal runaway is most likely to be realized when an event occurs that results in rapid heating of the cell that outpaces the rate of heat dissipation by the cell. Rapid heating may be caused by internal or external short circuits, overcharging, and general use as described in Chapter 2, or may be caused by heat from a source external to the cell, such as can be caused by radiant and conductive heating from adjacent cell heating, high ambient temperatures, and various types of mechanical shock. Each type of cell has a unique thermal profile that is dictated by the material properties of the components that constitute the cell, the mechanical construction of the cell, and the transfer of heat from the cell's case and conductors to the environment. The thermal and mechanical design of a cell strongly influences its ability to control and dissipate heat, thereby influencing its safety performance.

3.2.1 Thermal Design Considerations and Thermal Management

Heat propagation in Li-ion battery cells depends on several factors including the construction, the materials, and the location and type of the heat source as well as heat sinks. The heat from internal heat sources of any type of cell must reach the housing or the electrodes before it can be

dissipated to the environment. The materials and thickness of the outer packaging of the cell significantly affect the ability to dissipate heat. Failure to dissipate heat at a rate higher than the rate of heat generation in the cell could produce conditions for thermal runaway. Cylindrical cells depend heavily on a proper aspect (height to diameter) ratio to adequately dissipate heat. In a similar fashion, prismatic cells may have a limitation on cell thickness for heat rejection purposes.

Tab location also influences heat removal. For a given size prismatic cell, axial tab locations as opposed to radial tab locations generally exhibit improved thermal performance and more uniform thermal profiles (Pesaran, Heon, & Smith 2010). Based on this analysis, axial tabs allow for a more even distribution of heat throughout the cell and allow for larger tabs to be used to conduct heat out of the cell for a given cell size. One approach to prevent thermal runaway caused by current flow within the cell is to disable cell operation if the internal cell temperature exceeds a threshold limit. This can be done by including in the cell design a thermal shutdown separator, which loses its porosity as a result of partial melting at the temperature limit. If excessive heat builds in the cell from excessive charge or discharge rates or an external short circuit, the porosity of the separator is lost, which cuts off the flow of Li-ions and stops further current-induced heating. This safety feature, if activated, permanently disables the cell. If the heating is from SEI breakdown, high external temperature, or other causes not involving current flow (ionic transport), preventing ionic transport cannot prevent the exothermic reaction.

In the case of large format cells, Orendorff (2012a) explains that temperature variation across the cell leads to only a part of the separator shutting down, forcing the current through the remaining separator and accelerating the cell's failure.

Thermal management involves the methods and devices identified for charge and discharge management (since both can be considered thermal processes), as well as methods for dissipating the heat imparted to the cell by, for example, mechanical shock, vibration, and drop; and ambient temperature heating (Arora, Medora, Livernois, & Stewart, 2010).

Thermal management of ambient temperature heating is necessary to prevent undesired heating of the cell or pack during storage or operation. Temperature inside a vehicle on a hot summer day can rise above 100°F (Arora, Medora, Livernois, & Stewart, 2010). Thus, the Li-ion cells used in vehicles should be designed to function properly under these extreme conditions, or include cooling controls to ensure that the operational temperature range of the cell is maintained (Arora, Medora, Livernois, & Stewart, 2010). Ideally, these cells should be designed to perform in extreme cold and hot weather temperatures while both in use and in storage.

3.2.2 Mechanical Design Considerations

Each cell type has a different mechanical design and manufacturing process. The mechanical design influences the thermal characteristics of a cell, how the cells are assembled into modules and packs, resistance to mechanical damage, and the ability to withstand internal pressure without rupture. Cylindrical cells have a concentric circular standup of layers that are generally packaged in aluminum or steel cans, but other packaging types may also be in use. The cylindrical design inherently results in a symmetry that applies an even distribution of pressure on the layers of the cell; however, maintaining a uniform compressive force in prismatic cells is more challenging. Prismatic cells that do not have a rigid case are often packaged inside a case that provides structure and protection from shock, vibration, and other mechanical disturbances.

Protection against mechanical causes of failure should include isolating the internal components of the cell from direct exposure to mechanical abuse. This may be achieved through fabricating the cell or pack casing out of a high-strength material; however, there could be disadvantages to using such materials in that internal temperatures and pressures may be able to reach higher values before causing rupture. To protect against this, most Li-ion cells and packs are equipped with pressure vents to preclude casing rupture (Balakrishnan, Ramesh, & Kumar, 2006).

3.2.3 Charge and Discharge Management

Charging and discharging are the normal power cycles applied to Li-ion cells to either replenish or drain them of available electrical energy, respectively. Proper management of the electrical loads (i.e., electrical balancing) among cells in a pack helps maintain overall charge and discharge performance within an acceptable range, and prevent overdischarge or overcharge conditions. Because temperature is a key indicator of cell electrical performance (e.g., hotter cells may discharge or charge more quickly than colder cells), thermal management strategies are often integrated into the battery system design to monitor charging and discharging events and mitigate potentially problematic conditions (Bandhauer, Garimella, & Fuller, 2011), as discussed in Section 3.2.1. Such strategies often involve the use of liquid or air cooling mechanisms for packs of cells (Bandhauer, Garimella, & Fuller, 2011), as well as the cell-level devices discussed in Section 3.2.1.

At the cell level, charge and discharge management techniques need to take into account the states of charge of all individual cells within a pack. Inconsistency in capacity of individual cells within a pack is a significant performance and safety concern. The cell with the poorest capacity will limit the overall performance of the pack (Bandhauer, Garimella, & Fuller, 2011). Similarly, charging cells in series based on the capacity of the stronger cells, without a BMS to monitor individual cells, could overcharge the weaker cells, possibly causing cell damage or thermal runaway (Bandhauer, Garimella, & Fuller, 2011). Methods for addressing inconsistent capacities in packs are discussed in the following chapter.

3.3 Cell Safety and Failure Mitigation Measures

Each unique Li-ion chemistry, in combination with various cathode, anode, and electrolyte components, has a well defined usability range. When the cell and battery are operated within their designated charge and discharge regimes, and remain within appropriate ambient temperature ranges, the risk of cell failure is minimized. Conditions outside of the normal design parameters, unplanned “catastrophic effects,” or improper manufacturing techniques are factors that could lead to cell failure.

A failure inside a Li-ion cell or battery often results in more serious consequences than failures inside batteries with other chemistries. Catastrophic failure of Li-ion cells may be more severe than other rechargeable cells of equivalent size, because the Li-ion cell has a greater energy density and release rate and because the Li-ion cells contain flammable organic solvents as part of the electrolyte (Arora, Medora, Livernois, & Stewart, 2010).

Fire-safety concerns arise in Li-ion batteries primarily from the use of a flammable (organic) solvent component of the electrolyte, which could ignite if exposed to elevated temperatures or electrostatic sparks, and the lithiated SEI layer and anode when it is charged, which will erupt into flame if exposed to the moisture in the air. As discussed in Chapter 2, external short circuits, internal short circuits, cell overcharging, cell over-discharging, or exposure to high ambient

temperatures can each potentially cause overheating of a cell and initiate thermal runaway events, or weaken the cell such that it is more prone to thermal runaway (Arora, Medora, Livernois, & Stewart, 2010; Brenier, McDowall, & Morin, 2004). Manufacturing defects, such as contaminated materials, damaged electrodes, burrs, or weld spatter can also initiate thermal runaway events (Mikolajczak, Kahn, White, & Long, 2011).

Li-ion cell level protection is achieved primarily through the use of electrical components and subsystems to prevent heating and overpressure to the cell by opening the circuit, increasing resistance, or changing the chemical composition of the cell. These devices and subsystems include

- Standard and thermal fuses,
- Temperature cutoff (TCO) devices,
- Positive temperature coefficient (PTC) devices,
- Current interrupt devices (CIDs),
- Shutdown separators, and
- Vent disks or plugs (Balakrishnan, Ramesh, & Kumar, 2006).

Thermal fuses are designed to open when the cell temperature typically reaches 30 to 50°C higher than its rated operating temperature (Balakrishnan, Ramesh, & Kumar, 2006). They are relatively inexpensive and easy to install; however, they are prone to false triggers when normal operation includes pulse discharges and must be replaced after they are triggered. Standard fuses are also found in larger capacity battery cells where other current interrupting devices may not be practical. As an alternate to fuses, other circuit breaker-based devices such as TCOs and PCMs operate on the same temperature-sensing principles but can be reset after triggering (Balakrishnan, Ramesh, & Kumar, 2006). TCOs are usually wired in series with the cell or cell pack, while PCMs are usually separate modules attached to the cell or pack (Balakrishnan, Ramesh, & Kumar, 2006). The main disadvantages to using TCOs and PCMs are their size and cost.

Self-resetting PTC devices operate by exploiting materials whose resistance increases with temperature. At normal operating temperatures the PTC resistance is low, but in the presence of high temperatures the resistance increases exponentially. Thus, when an external electrical stimulus such as a short circuit results in rapid heating of the PTC element, the PTC responds with an increase in its resistance, thereby reducing the flow of current. When the stimulus is removed, the PTC cools and self-resets. PTCs typically trigger at temperatures in excess of 100°C and can be used several times before they cease to reset. When the PTC fails, it remains in its high-resistance state, preventing operation of the cell until the PTC is replaced (Balakrishnan, Ramesh, & Kumar, 2006). PTCs may not be practical in large cells and do not protect against all types of external short circuits. PTCs are not commercially available for large cells or for prismatic or pouch cells. If the short circuit resistance is above a certain value, the PTC may never heat up enough to reach the trip point before the cell fully discharges. In this type of situation, the cell must have other methods of protection or depend on adequate heat transfer to ambient to prevent overheating of the cell. This type of overheating can lead to degradation of the cell rather than immediate thermal runaway (Pesaran, Kim, Smith, & Darcy, 2008).

It has also been shown that PTCs can fail in situations where multiple cells containing PTCs have been stacked in a single series string to create high voltages (Cowles, Darcy, Davies, Jeevarajan, & Spurrett, , 2002). In this type of configuration the first PTC in the series string to

trip could be exposed to the entire voltage of the string. This overvoltage may exceed the rating of the PTC, causing a failure or damage to the device. In order to mitigate this problem, diodes can be placed in parallel with single cells or groups of series cell. The purpose of the diodes is to limit the maximum voltage across tripped PTCs by shunting fault current. This strategy allows the PTCs to trip in succession and if properly designed ensures that none of the PTCs exceed their voltage limits.

CIDs are primarily used to protect the cell when mild overpressures are caused by cell abuses such as overcharging. CIDs are activated from increased pressure inside the can, which breaks the contact between the cathode and cap in an attempt to break the current path and stop the reaction. If the flow of charge is not the source of the overpressure and pressure continues to build, vent disks or plugs are used in the cell design to expunge the electrolyte in a semi-controlled manner and thereby stop the cell from heating any further. The exhaust vent is generally the final protective measure, and if it does not operate quickly and properly then the cell will likely fail violently.

Some cell designs use a chemical protection scheme known as a shutdown separator. In these cells, the separator is designed to melt in such a way that it fills the pores that allow current to flow, thereby stopping the chemical reaction. The separator is designed to shut down at a lower temperature than the thermal runaway temperature (Baldwin, 2009).

3.4 Potential Li-ion Cell Failure Hazards

The objective of this section is to discuss possible hazards and toxicity concerns, assuming that safety features or controls are unable to prevent or mitigate them. Designers should be aware of potential hazardous conditions that should be addressed in battery design. Although *possible* hazards are discussed, the *likelihood* of realizing the conditions creating these hazards may be low; however, even low-likelihood events cannot be ignored when designing a Li-ion battery, because of the severity of potential consequences.

Battery cells are a multi-physics combination of electro-chemistry, electrical, mechanical, and thermal processes. For each battery chemistry, design, and expected duty cycle, there is a range of temperatures and range of operating voltage in which electrochemistry is dominated by intercalation mechanisms described in Chapter 2. Outside this range, undesirable exothermic reactions side reactions and/or internal electrical shorts (excessive flow of electrons) may occur, both of which can lead to self-heating. Exothermic reactions and/or internal electrical shorts may be triggered by manufacturing defects, or mechanical, electrical, or thermal errors, misuse or abuse (Arora, Medora, Livernois, & Stewart, 2010). If allowed to continue, these reactions or shorts can create conditions for self-heating within the cell; which grow to become uncontrolled increases in temperature and pressure (thermal runaway); and potentially end in venting or catastrophic failure of the cell. Surrounding cells may be affected by elevated temperature and pressure, and cell failure, with the potential for propagation beyond the individual cell.

The potential primary hazards associated thermal runaway induced heat and pressure include

- Venting of high-temperature electrolytic solvent vapors, either through pressure relief devices or holes in the casing
- Combustion and flammability of ejected flammable electrolytic solvent vapors
- Local atmospheric overpressure

If pressure relief devices are not present or if they fail, then primary hazards may also include

- Cell casing rupture and release of projectiles

The heat and pressure resulting from thermal runaway, as well as combustion of solvent vapors and local overpressure may create conditions for self-heating within adjacent cells, particularly if they are damaged by the similar defects, errors, misuse or abuse that damaged the first cell. Consequently, the potential exists for propagation of thermal runaway throughout a series of cells within an array and module. The severity and consequences of particularly hazard are clearly multiplied through propagation beyond a single cell.

Potential secondary hazards that develop as a consequence of the primary hazards may include

- Toxic and incompatible (corrosive) materials
- Asphyxiation
- Ignition and burning of adjacent flammable vehicle components or surfaces
- High-voltage electrical shock hazards, (due to melting or burning of electrical insulation and isolators)

Secondary effects may have their own associated thermal and overpressure effects.

3.4.1 Primary Combustion and Flammability Hazards

Several flammable or combustible chemicals are or could be present in Li-ion batteries, including those required for battery operation as well as the products of chemical reactions associated with internal failure processes within the battery. For combustion of these chemicals to occur, three elements must be simultaneously present: fuel, oxygen, and an ignition source. Premixed flames require that the fuel and oxygen exist in the vapor state and be in proper proportions, i.e., within the flammability limits. For diffusion flames, combustion is characterized by the molecular and turbulent diffusion rates of the oxygen and fuel (Glassman 1977). In either case, *local* concentrations of fuel and oxygen are critical for initiating and sustaining a combustion reaction, even in situations where *global* concentrations appear to not favor combustion. Two of the elements could be present prior to or during battery casing rupture: (1) flammable liquids, gases, hydrocarbons (liquid and solid), and metals (fuels) are either inherently present or can be formed upon failure; and (2) oxygen is available in the ambient air, or can be formed within the battery as a result of decomposition reactions associated with internal failure; however, evidence of combustion reactions occurring inside of the battery as a result of oxygen generated within the cell have not been reported to date (Mikolajczak, Kahn, White, & Long, 2011). The required ignition source could be in the form of hot surfaces, hot-metal sparks, internal battery shorts, exposed vehicle electrical wiring, or rupturing of the cell packaging.

Any specific flammability hazard is best qualified by identifying the flammable chemicals present in Li-ion batteries or produced as a result of battery failure processes, and compiling

comparative data on the combustion parameters for each. These data, primarily taken from MSDSs, are summarized in Table 3-1. They are organized by fuel classification: flammable gases; flammable electrolytes; and metals, and includes the following characteristics:

- Flash point: the minimum temperature at which a substance is present in ignitable concentration (requires an external energy source, such as a spark)
- Auto-ignition temperature: the lowest temperature at which a substance can autoignite
- Flammability limits (lower and upper): the concentration regime (with respect to air) between which a combustible gas is flammable
- Energy value: the reaction heat of combustion (kilojoules, kJ) on a per volume (liters, L, for gases and electrolytes) or per mass (kilograms, kg, for metals) basis.

Table 3-1. Flammable materials associated with Li-ion battery operation or failure.

Classification	Chemical	Flash Point (°C)	Auto-Ignition Temperature (°C)	Flammability Limits		Energy Value (kJ/L)
				Lower (%)	Upper (%)	
Flammable Gases	Hydrogen (H ₂)	Gas	520	4	75	12.8
	Ethylene (C ₂ H ₄)	Gas	450	2.3	28.6	61.9
	Ethane (C ₂ H ₆)	Gas	510	3	12.5	69.6
	Propene (C ₃ H ₆)	Gas	460	2	11.1	79.6
Flammable Electrolyte Solvents	EC (C ₃ H ₄ O ₃)	143	465	3.6	16.1	17
	DMC (C ₃ H ₆ O ₃)	18	458	4.2	12.8	16
	PC (C ₄ H ₆ O ₃)	132	510	1.8	14.3	20
	DEC (C ₅ H ₁₀ O ₃)	25	445	1.4	11	21
Metals ^a	Lithium	High	≈179	43 (MJ/kg)
	Aluminum	High	≈760			30 (Mj/kg)
	Copper	High	≈700			16.9 (kJ/kg)

EC = Ethylene carbonate

DMC = Dimethyl carbonate

PC = Propylene carbonate

DEC = Diethyl carbonate

a. Only very small quantities of lithium and aluminum have been reported to be ejected from failed batteries (Mikolajczak, Kahn, White, & Long, 2011).

The flammable gases H₂, C₂H₄, C₂H₆, and C₃H₆ are typically formed from failure processes occurring within a compromised battery, which were discussed in Section 2.3 above. These gases exhibit: (a) relatively high diffusivity; (b) low concentrations in the local atmosphere that approach or exceed the Lower Flammability Limit; and (c) low flash points (compared to ambient or operating temperatures). These gases should therefore be considered the most

significant flammability threats of the entries in Table 3-1; however, some form of internal failure mode must occur for these gases to form.

Flammable electrolyte solvents are inherently present in Li-ion batteries and are required for the battery to function. The four most common Li-ion battery solvents are listed in , along with data pertaining to their flammability. These materials should be also be considered a significant flammability threat, because they are always present in the battery or could degrade into potentially hazardous products (i.e., the flammable gases in Table 3-1). However, their threat of ignition and fire is not as severe as the flammable gases, mostly because of their flash point temperature requirement. These electrolyte solvents will not have a high concentration in the vapor phase at temperatures lower than the flash point temperature and will not be able to form ignitable mixtures in air. All of the solvents listed in Table 3-1, with the exception of DMC and to some extent DEC, have flash points above room temperature (20° to 25°C [68° to 77°F]).

Metallic lithium is formed primarily through dendritic growth. Decomposition of lithium-containing chemicals, such as LiF, Li₂CO₃, or the battery anode and cathode to lithium has been hypothesized; however, these reactions are reported to occur only at extremely high temperatures, with frequencies of these reactions not well understood (Spotnitz & Franklin, 2003). Further, formation of lithium at elevated temperatures would require a very strong reducing atmosphere that is not present in the cell. If battery chemicals that contain lithium do not decompose and are expelled during failure, they cannot be considered a flammability hazard, but could be a plausible material compatibility or toxicity threat. The lithiated carbon in a charged anode, the SEI layer, and any free lithium that might be present (due to dendrites or overcharging and plating) represent the greatest flammability threat in a Li-ion cell. While lithium is non-volatile (i.e., flash point will not be a concern), the table fails to take into account the reactivity of finely divided lithium. A lithiated anode will burst into flame when exposed to moist air. The reaction with water produces H₂ and as characteristic of many metals, it releases significant heat during oxidation (combustion) and ignites the H₂.

Any flammability hazard assessment should also take into account the availability of oxygen within and outside of the cell. In battery casing failure conditions, oxygen is always available in the surrounding ambient air (at a volume percentage of 21%) and can participate in combustion reactions with expelled flammable battery materials, provided that ignition sources are present. In instances where the battery exhibits internal failure conditions, but the casing remains intact, oxygen could be produced as a result of chemical decomposition reactions caused by internal failure processes in the battery. Within the battery, this oxygen could react via premixed or diffusion-driven combustion reactions with the flammable gases and electrolyte solvents shown in Table 3-1. However, the probability of this internally generated oxygen participating in any combustion reactions within the battery appears to be very low: evidence of such internal combustion reactions has not been reported in the technical literature (Mikolajczak, Kahn, White, & Long, 2011). In either the internal or external combustion scenario, a minimum oxygen concentration must be present for combustion to occur. Table 3-2 provides the minimum oxygen requirements for each of the flammable chemicals

Chemical	Minimum Oxygen Concentration (%)
H ₂	5
C ₂ H ₄	6.9
C ₂ H ₆	10.5
C ₃ H ₆	9
EC	9
DMC	7.2
PC	12.6
DEC	8.4

Table 3-2. Minimum oxygen concentration for lithium-ion battery flammable chemicals.

listed in Table 3-1. For diffusion-driven combustion, the oxygen will be transported to the fuel via molecular and turbulent diffusion, and, consequently, no specific premixed proportional ratio of oxygen and fuel is required for combustion to occur. For both types of combustion, it is important from a safety standpoint to take into account the global and local quantities of oxygen and flammable materials. Even if the minimum oxygen conditions provided in Table 3-2 are satisfied on the global level (e.g., the global concentration of oxygen within a battery is 3% by volume), this oxygen could undergo combustion reactions with fuel if some *local* concentration of oxygen is (a) mixed with a *local* concentration of fuel at flammable proportions (for premixed combustion) or (b) allowed to diffuse into the fuel (for diffusion combustion). Therefore, both global and local oxygen and fuel concentrations should be taken into account for safety purposes and failure analyses.

3.4.2 Secondary Toxic and Incompatible Materials Hazards

Toxic and incompatible materials include all battery chemicals and byproducts that are toxic or corrosive by themselves or react with other materials to produce toxic, flammable, or heat-generating chemicals. The information contained in this section was taken from technical reports on toxic and incompatible chemicals (including byproducts) commonly present in Li-ion batteries or formed during failure (Yang, Zhuang, & Ross, 2006), along with available MSDSs. Data are discussed on the incompatibility and toxicity of the chemicals contained in a Li-ion battery whose integrity has not been compromised and then of the products associated with the decomposition of these chemicals.

Table 3-3 summarizes data on the key components of a Li-ion battery. For each component there are, in some cases, several options for the specific component chemistry; complete lists of all component chemistry options were provided in Section 2.1. Regardless, each category of options presented in shares common health effects, material incompatibilities, and flammability characteristics. The toxicity and incompatibility of a specific chemical should be found in the MSDS and other safety information.

Table 3-3. Health, material incompatibility, and flammability data for Li-ion battery components.

Component	Examples	Health Effects	Incompatibilities	Flammability
Cathode	Lithium Cobalate (LiCoO ₂); Lithium Manganate (LiMn ₂ O ₄); Lithium Phosphate (LiFePO ₄)	Eye, skin, respiratory, and gastrointestinal irritant; possible carcinogens	None, but avoid extreme heat and fire	Non-flammable
Anode	Graphite (C)	None in solid form (avoid dust)	None, but avoid extreme heat and fire	Non-flammable
Electrolyte Salt	Lithium Hexafluorophosphate (LiPF ₆)	Causes burns to eyes, skin, gastrointestinal tract, and respiratory tract	Water; oxidizing agents; strong acids	Non-flammable
Electrolyte Solvent	EC; DMC; PC; DEC	Eye, skin, respiratory, and gastrointestinal irritant	Oxidizing agents; acids; alkalis	Flammable
Separator/Binder	polyethylene; polypropylene	None reported	None, but avoid extreme heat and fire	Non-flammable

Reviewing the data in Table 3-3, the cathode component appears to pose significant toxicity risks. However, the chance of human exposure to these chemicals could be considered low because these components are solids that possess high melting temperatures. Exposure to these chemicals would require the rupture of a battery with fragmentation or vaporization of the component chemicals, which is unlikely.

The more hazardous chemicals inherently present in a Li-ion battery are the SEI layer (containing lithium) and the lithiated carbon anode plus those comprising the electrolyte salt and electrolyte solvent. In the majority of Li-ion battery designs, the electrolyte salt (LiPF₆) is dissolved in the electrolyte solvent (EC, DMC, PC, or DEC); therefore, the more likely hazard would be ejection or leakage of electrolyte fluid from the battery. The primary hazards with the electrolyte solvents are the health effects listed in and the flammability hazards discussed. The combustion of any of the electrolyte solvents would also yield water (H₂O), which may influence the degradation of the LiPF₆ salt, and the asphyxiates CO and CO₂.

The primary hazards with the electrolyte salt LiPF₆ are the health effects noted in , and its incompatibility with water, which yields lithium fluoride (LiF), phosphoryl fluoride (POF₃), and hydrofluoric acid (HF) by the following reaction (Yang, Zhuang, & Ross , 2006):



These toxic or corrosive LiPF₆ decomposition products will be discussed in detail.

If failure processes associated with thermal runaway occur within the battery, several hazardous chemicals may also be produced from various reactions. These reactions were discussed above, and include reactions between the chemicals comprising the SEI and the electrolyte solvents;

internal electrolyte solvent combustion; and cathode decomposition. The significant hazardous products formed in these reactions include the flammable hydrocarbons presented in (C_2H_4 , C_3H_6 , and C_2H_6); flammable gases and/or asphyxiates (H_2 , CO_2 , and CO); and LiF . Water can also be produced from the combustion of the electrolyte solvents, which could contribute to the formation of HF , POF_3 , and additional LiF . The toxicity and incompatibility data for these three chemicals are summarized in , which is similar to the analysis performed for the data in .

The primary hazards with LiF are its toxicity if ingested or inhaled and its incompatibility with water. Contact with water can result in the formation of HF , one of the other hazardous materials listed in Table 3-4. The primary hazards with HF are its extreme toxicity and corrosiveness and its incompatibility with metal, glass, and rubber (common vehicle materials), which subsequently release flammable hydrogen gas upon contact. Little to no data exist on the specific toxicity and incompatibility of POF_3 . The data presented in Table 3-4 were based on a phosphoryl chloride ($POCl_3$). POF_3 is assumed to have similar toxicity effects and material incompatibilities as $POCl_3$ given that both chemicals possess a halogen (chlorine or fluorine) and phosphorus.

Table 3-4. Health, incompatibility, and flammability data for Li-ion battery byproducts.

Component	Health Effects	Incompatibilities	Flammability
LiF	Eye and skin irritant; toxic if swallowed or inhaled	Water; acids; oxidizing agents	Non-flammable
HF	Extremely hazardous (irritant, corrosive) to skin, eyes, and internal organs upon ingestion or inhalation.	Metals; organic materials; alkalis; glass; ceramics; corrosive to most substances	Non-flammable, but can release flammable gas
POF_3	Not available, but most likely extremely hazardous	Not available, but most likely incompatible with water; metals; and strong bases	Non-flammable

3.4.3 Secondary Asphyxiation Hazards

Asphyxiation is a possible hazard resulting from venting or ruptured Li-ion batteries within a vehicle trunk or passenger compartment⁴; furthermore such risk is directly proportional to the number of venting cells and amount of gases effused and the rate of vehicle air changeover. Therefore, asphyxiation could be most likely to occur when the battery casing has been compromised and there is little to no opportunity for external venting or air changeover within the vehicle (e.g., in a vehicle crash in which the windows remain intact in the up position and doors are closed). Therefore, the probability of asphyxiation occurring may be low. Nonetheless, the Li-ion battery designer should be aware that the MSDS for known asphyxiates state that the symptoms of asphyxiation (dizziness, nausea, etc.) can occur when oxygen levels are less than approximately 19.5%; levels under 8 to 10% can bring about rapid unconsciousness.

Chemicals that pose the highest threat of asphyxiation are the gases that are released when the battery casing is compromised through venting or rupture. These gases—namely H_2 , C_2H_4 , C_2H_6 , C_3H_6 , along with carbon dioxide (CO_2) and carbon monoxide (CO) produced from combustion—

⁴ While large Li-ion batteries are commonly mounted outside the passenger compartment, some small batteries in mild hybrid vehicles have been mounted in a trunk or under the cargo area of SUVs that are not isolated from the passenger compartment.

displaces the ambient vehicle air. The threat of asphyxiation is also present for the volatile electrolyte solvents in Table 3-3. The concentrations of these solvents in the vapor phase are fluid and temperature dependent; therefore some solvents may be considered a higher asphyxiation threat than others. For both the gases and solvents, the specific threat of asphyxiation is a function of the quantities of the chemicals released, their release rate, and the degree of accumulation in the vehicle. Most of the asphyxiates produced as a result of Li-ion battery failure are also flammability hazards, and can be present in both the flammability and asphyxiation ranges at the same time.

3.4.4 Secondary Ignition of Adjacent Flammable Vehicle Components and Surfaces

Although not explored in this investigation it is observed here that the primary hazards including venting and combustion of high-temperature electrolytic solvent vapors and ejection of hot casing particles or projectiles have the potential to ignite adjacent vehicle components and surfaces, creating additional hazards for occupants and first responders.

3.4.5 Secondary High-Voltage Electrical Shock Hazard

High-voltage electrical shock is a potential secondary post-crash and post-fire safety hazard. The high-voltage electrical bus on Li-Ion battery and plug-in hybrid vehicles⁵ typically operate at a few hundred volts, well above the thresholds of 60 VDC and 30 VAC considered safe by electrical vehicle safety standards. (GTR HFV, 2011 Draft [2011]; NHTSA Response. NHTSA-2011-0107; 49 CFR 571.305 ; SAE J2578 [2009]). It is well known that a crash can damage electrical insulation and isolation systems. Additionally a thermal event caused by Li-ion cell or battery overheating could melt or combust electrical insulation and isolators, potentially allowing occupants, maintenance personnel or first responders to contact high-voltage components. This hazard is present on all high-voltage systems and is not limited to Li-ion battery vehicles. A substantial body of research exists on this topic and vehicle safety codes and standards appear to have achieved consensus on safety requirements, described in more detail in Section 10.2.5 of this document.

3.5 References

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⁵ Li-ion batteries have also been observed as temporary energy storage devices on fuel cell vehicles electrical systems.

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4 Li-ion Battery System Architecture

Chapters 2 and 3 of this report described the chemistry, electrochemistry, construction, and safety considerations for Li-ion cells, and the fundamental building block for Li-ion batteries. A cell is the basic unit in a battery that produces a voltage and a current. A single cell cannot store enough energy to power a motor vehicle, so cells are grouped into arrays, modules, and packs, along with control systems, to form the complete battery package.

This chapter describes a *potential generic* design methodology for complete Li-ion battery systems. It presents the architecture for joining cells to form a module and for joining modules to form a complete battery pack. To achieve the necessary performance and safety requirements, a module and pack also contains control electronics and other components.

This chapter also presents a potential generic Li-ion battery design from the cell up to the complete battery pack. This chapter serves two purposes: it informs the reader how a battery system *may* be constructed, and it provides a generic design that is used as the basis for analysis and discussion in subsequent chapters of the document. A number of different design strategies have been undertaken by manufacturers. There is no single universal design strategy and some choices are the subject of debate within the industry. Where possible, different options for design are identified.

In developing the Li-ion battery design in this chapter, many design choices were made that influence performance, cost, and safety. Battery manufacturers and vehicle integrators must trade-off between these three competing objectives at each step of the design process. The process shown here specifically emphasizes safety. This is done to show where safety elements may be incorporated in a system and supports an assessment for situations where one of these devices fails. Manufacturers address safety issues for their specific battery system, while this is a generic design. A manufacturer's decision not to include a safety feature shown here does not imply that that design is unsafe or less safe. It only implies a difference in approach and objectives for this investigation.

Finally, this chapter describes the detailed integration of Li-ion cells into battery modules, followed by the integration of modules into battery packs. Chapter 5 compares the characteristics of battery packs used in HEVs, PHEVs, and BEVs.

4.1 Battery Modules

A typical module consists of an array of cells, sensors, controls, protective safety devices, structures and mounts, cooling elements or cooling provisions, and communications capabilities. This section describes module composition, module operation, and control by building a model of a typical battery module in a step-by-step manner.

Connecting lithium batteries is complicated. Variation of individual cell capacity is the primary complication. This variation could result from manufacturing differences, stress, aging, and other environmental variables. A weak cell cannot accept the same level of charge as a strong cell and will exhibit slightly different electrochemical characteristics. Incorrectly charging a weak cell can lead to overheating, and potentially a fire. The module architecture and a BMS address these issues.

4.1.1 Cell Arrays

The available voltage from one cell is limited by its chemistry. Electrochemical material properties limit lithium cell voltages to 3 to 4 volts. The voltage requirements for most BEV or HEV systems are in the range of a few hundred volts. Cells must be connected in series to achieve the required operating voltages. Cell arrays are connected in parallel to meet high electrical current and power requirements.

An array of cells can be configured in series, parallel, and series-parallel configurations. These configurations are selected to meet system-level voltage, current, power, and energy requirements.

4.1.1.1 Series Arrays

A series array of battery cells is a nose-to-tail string of two or more cells, as shown with cylindrical cell representations in Figure 4-1. A weak cell in a series array will charge more quickly than a strong cell. With lithium battery chemistries, it is not safe to continue to charge a weak cell so that a strong cell can receive a full charge. Overcharging the weak cell makes that cell less stable, and can lead to overheating. The state of charge for each cell must be monitored to prevent overcharging a cell within a series array to protect the cell and the array, as illustrated in Figure 4-2. If the entire series array is to be fully charged, cell balancing techniques are required.



Figure 4-1. Series array with a weak cell.

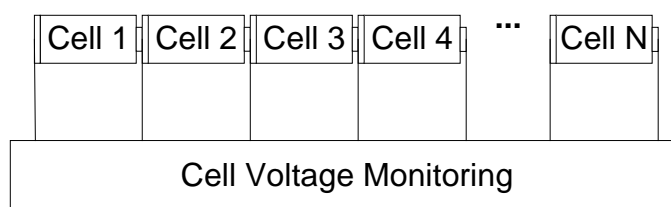


Figure 4-2. State of charge monitor needed for series array.

Cell balancing is a technique used to safely bring each lithium battery in a series array of weak and strong cells to a full state of charge.

A circuit is needed to control the charge of each cell. Many circuit possibilities exist. Active circuits require more parts but provide higher efficiency. Dissipative balancing circuits have fewer parts but convert overcharge currents to heat and so are less efficient. A dissipative circuit is described in this safety based assessment for simplicity. Typically this circuit is a chain of transistors and resistors configured in parallel with the cell series. An example charge control circuit is shown in Figure 4-3. As the batteries charge or discharge, the parallel resistor-transistor circuit turns on and off to manage or balance the state of charge of the entire battery array. These circuits maximize the available battery array charge. A controller is needed to monitor cell voltages and determine when to switch the transistors on and off.

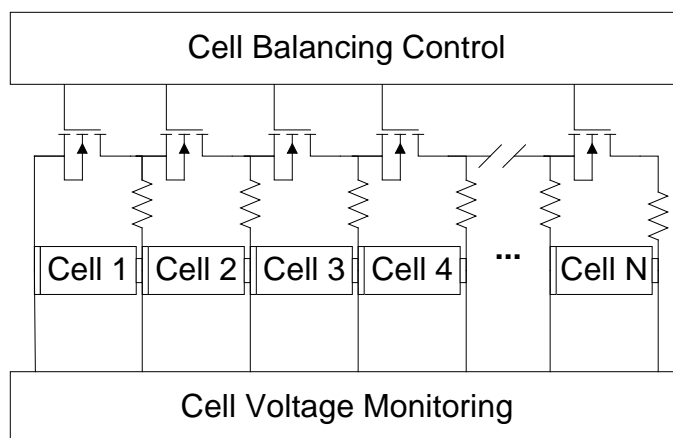


Figure 4-3. Series battery array with a charge control.

4.1.1.2 Parallel Arrays

A parallel array of battery cells is a nose-to-nose and tail-to-tail battery connection. As with the series array, cell-to-cell differences are problematic. Weak cells have a higher internal resistance than strong cells. The weak cell will reach full charge sooner than the strong cells, but the parallel connection does not allow monitoring of individual open circuit cell voltages. A parallel connection of cells without additional circuit elements could possibly result in cell damage. Parallel cells can be isolated from each other with diodes, as illustrated in Figure 4-4. However, the isolating diodes complicate recharging (Figure 4-5), and the forward diode voltage reduces the efficiency of the array. Industry comments suggest that some manufacturers implement parallel arrays of cells without isolation and that this is an ongoing topic of discussion. Testing would be necessary to further compare and contrast the two approaches.

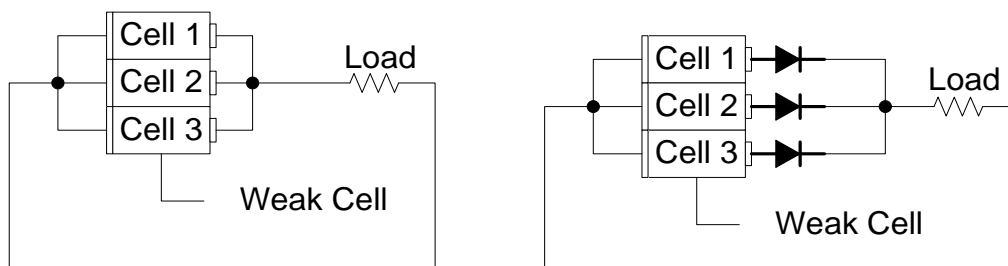


Figure 4-4. Diodes prevent weak cells from loading strong cells.

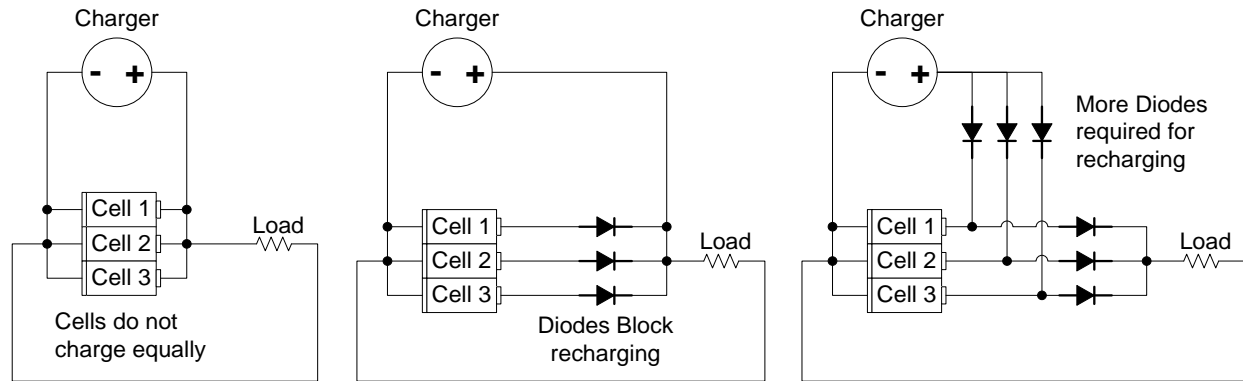


Figure 4-5. Diodes complicate recharging.

This report must choose either a parallel or series configuration to develop a design for subsequent analysis. A parallel array of series cells, illustrated in Figure 4-6, was chosen as the basis for subsequent design. The PASC requires only two sets of diodes at the positive (or negative) PASC terminal, as shown in Figure 4-7. The PASC configuration reduces the forward voltage drop across isolation diodes. The authors recognize that there are design tradeoffs for either a PASC or a series array of parallel cells. PASC was chosen as the most practical for this study, but it is not the best or only solution for all cases.

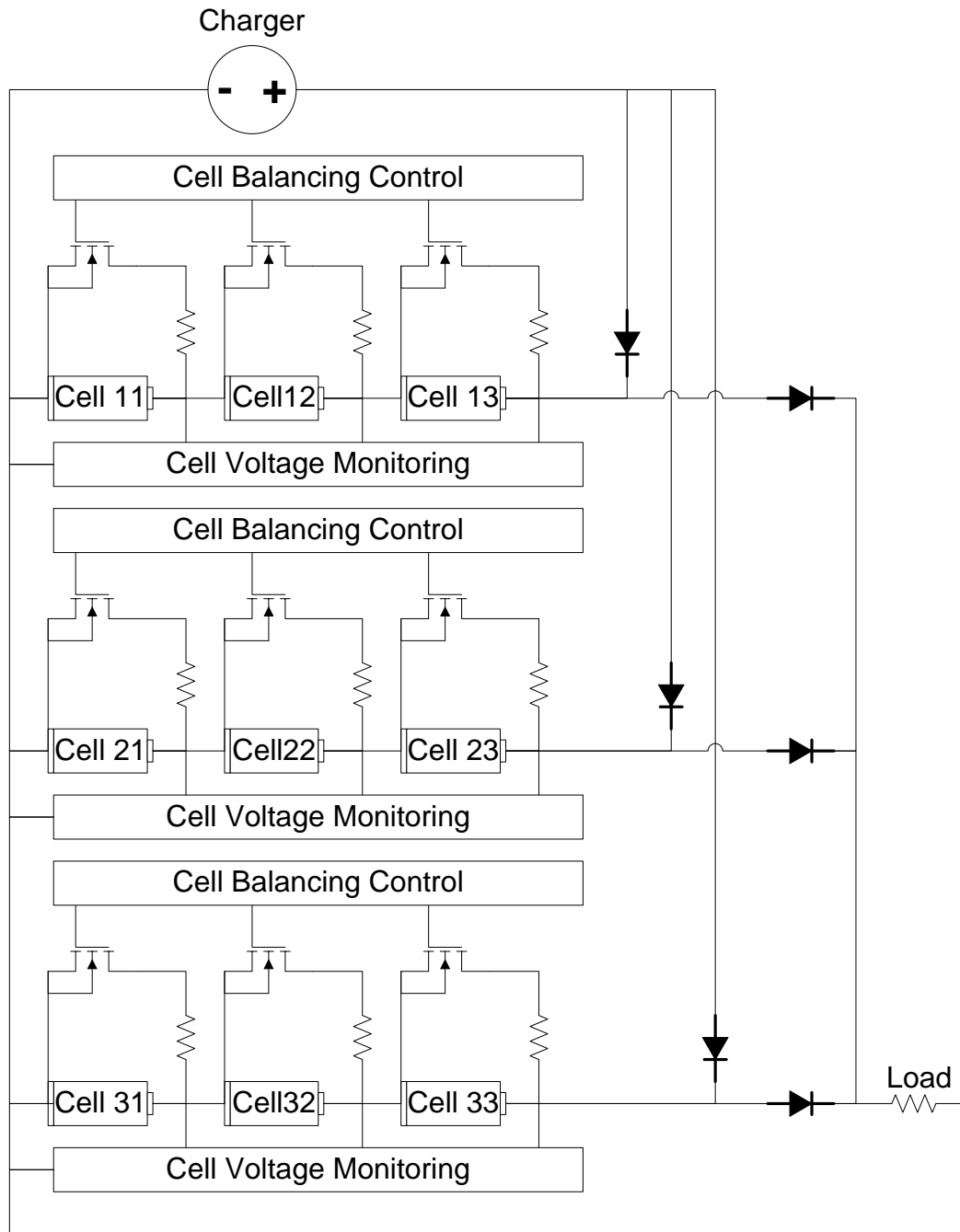


Figure 4-6. Parallel array of series cells.

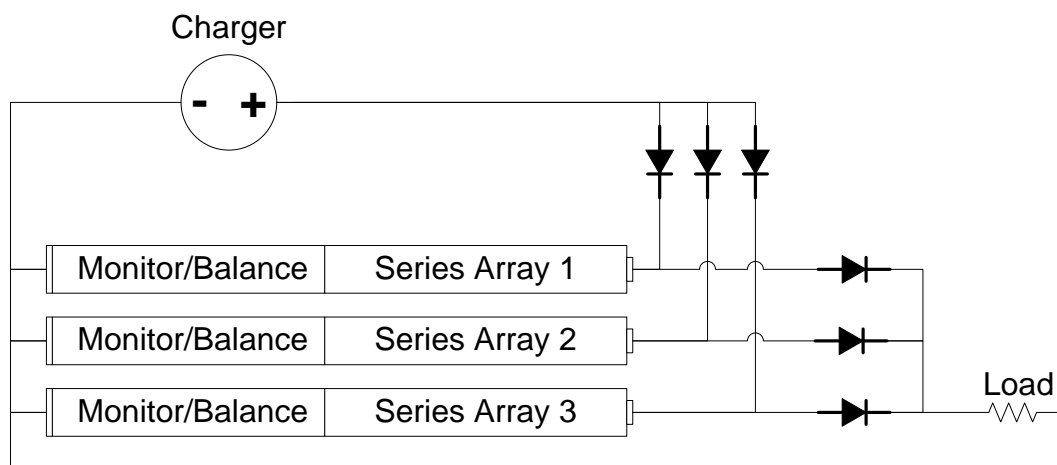


Figure 4-7. Simplified parallel array of series cells.

4.1.2 Charge and Discharge Management

Charge and discharge management is a means of limiting the electrical current to and from the module or series arrays within a module. Limiting discharge rate reduces stress and improves battery life.

Normal discharge current may be for traction or accessories. Traction current is highest during acceleration and much lower during normal drive. Accessory current demands are much lower but may have high in-rush demand, though this is lower than traction acceleration current. Recharging current may be from braking, an onboard generator, or plug-in power from a stationary outlet.

Battery module design must also address the potential for abnormal discharge. Abnormal discharge may be caused by failures such as internal or external short circuits.

4.1.2.1 Active Current Limiting

The design of the overall vehicle system and battery pack should limit charge and discharge rates by design. However, the battery module should include a current limiting device or circuit to further protect the cells. A simple, representative active current limiting circuit and generalized current limiting symbol are shown in Figure 4-8. In this circuit, bias and sense resistors are selected to set a current at which transistor, Q1, begins to drop more voltage, thereby limiting the current. As the current through the sense resistor increases, the Collector-Emitter voltage in transistor Q2 increases and eventually turns on Q2. After Q2 turns on, it sinks current through the bias resistor and reduces the current in the C-E junction of transistor Q1. Reducing the C-E junction current limits the current that can pass through Q1. The setpoint for the limit is defined by the cell current limit for the module or a series array. The circuit in the figure only supports unidirectional current limiting; other more complex circuits and techniques may be used in a battery module. The generalized symbol in this figure is intended to represent any current limiting circuitry that might be in use and this generalized symbol will be used in the remainder of this analysis.

PASC could have a current limiter on the output, as shown in Figure 4-9. A current limiter for each series array in the module, as shown in Figure 4-10, would provide greater protection.

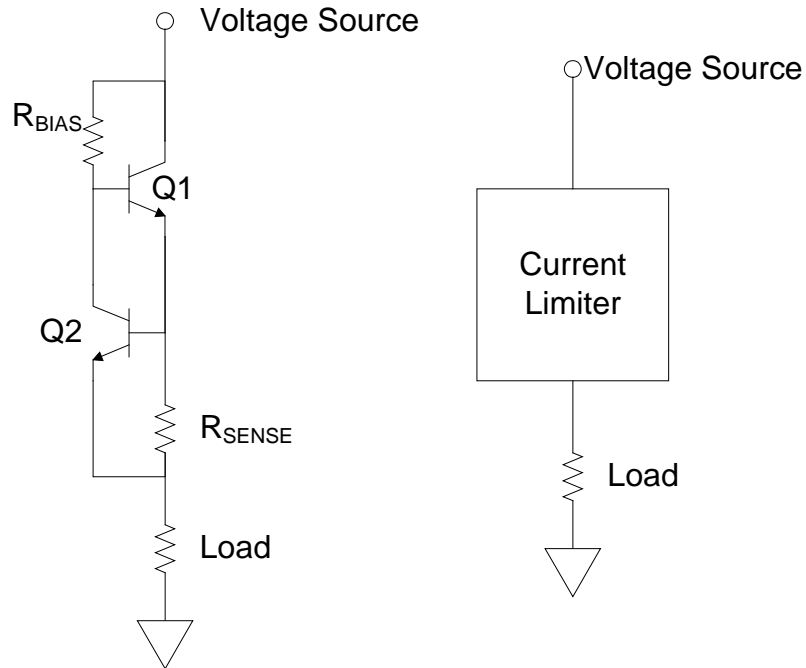


Figure 4-8. Simple current limiting circuit and general symbol.

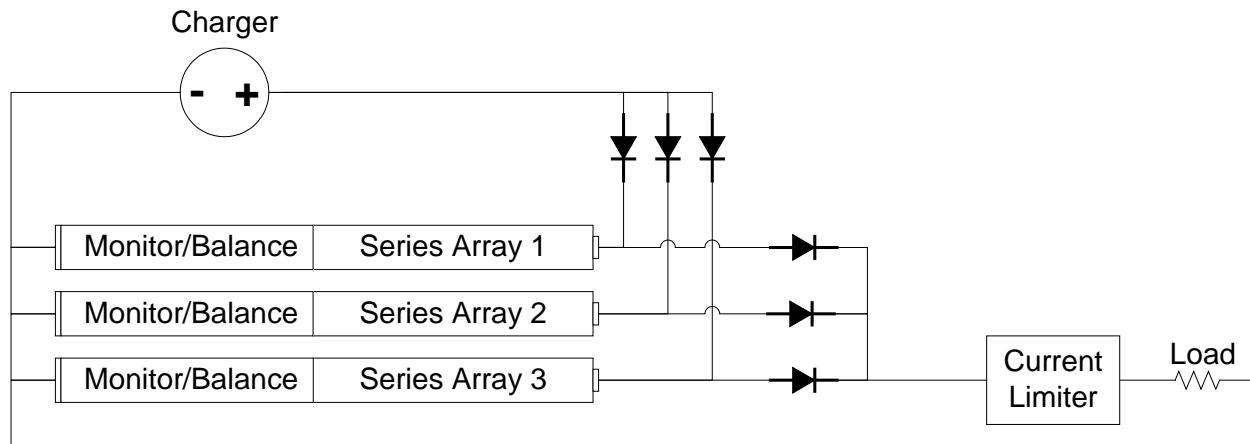


Figure 4-9. Battery module with one current limiter per module.

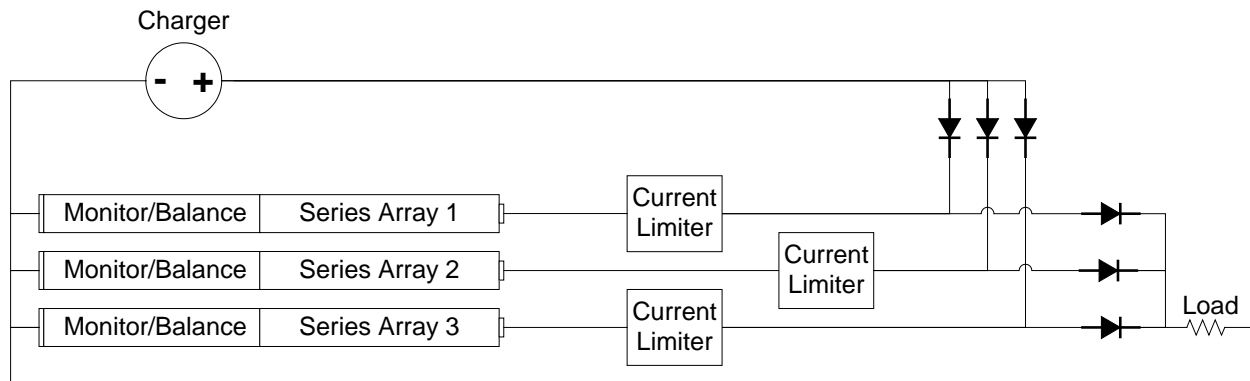


Figure 4-10. Battery module with one current limiter per series array.

4.1.2.2 Current Limiting by Fuse or Circuit Breaker

Fuses and circuit breakers are well known current limiting devices. Fuses are one time, fail-safe devices. If the current exceeds the fuse rating for a long enough duration, the fuse element will burn and the circuit becomes disconnected, thereby protecting the cells in a module from extreme overcurrent conditions. Circuit breakers perform the same function but are resettable.

Like current limiters, fuses may be connected in series with the module (Figure 4-11) output or in each series array (Figure 4-12) within a module.

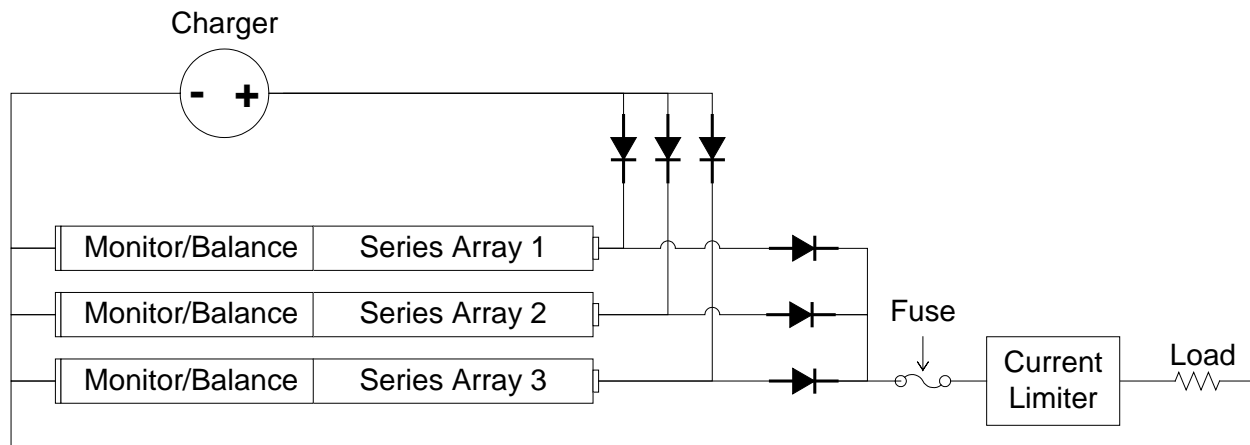


Figure 4-11. Battery module with one fuse per module.

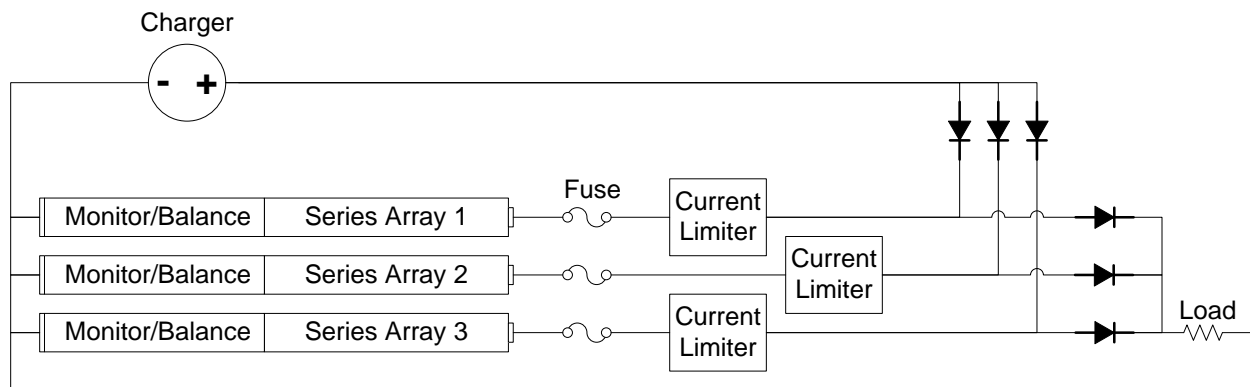


Figure 4-12. Battery module with one fuse per series array.

4.1.2.3 Charge and Discharge Current Monitoring

The charge and discharge current may be used in conjunction with control circuits as a third means to protect module cells from undesirably high currents.

Like current limiters, current monitors may be connected in series with the module (Figure 4-13) output or in each series array (Figure 4-14) within a module. These outputs can provide charge and discharge current data to state-of-health (SOH) and state-of-charge (SOC) algorithms. The monitored current level can be used to open a power contactor switch, interrupting the flow of current and protecting the module, as shown in Figure 4-15.

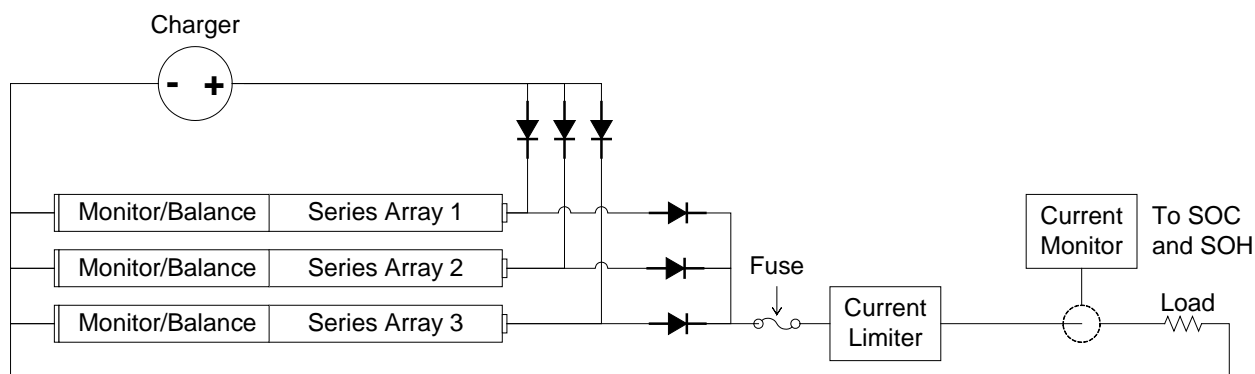


Figure 4-13. Battery module with one current monitor per module.

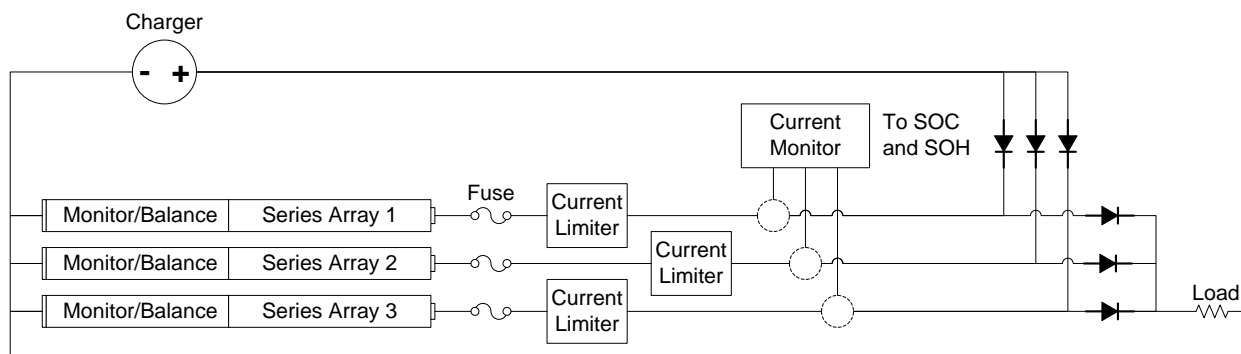


Figure 4-14. Battery module with one current monitor per series array.

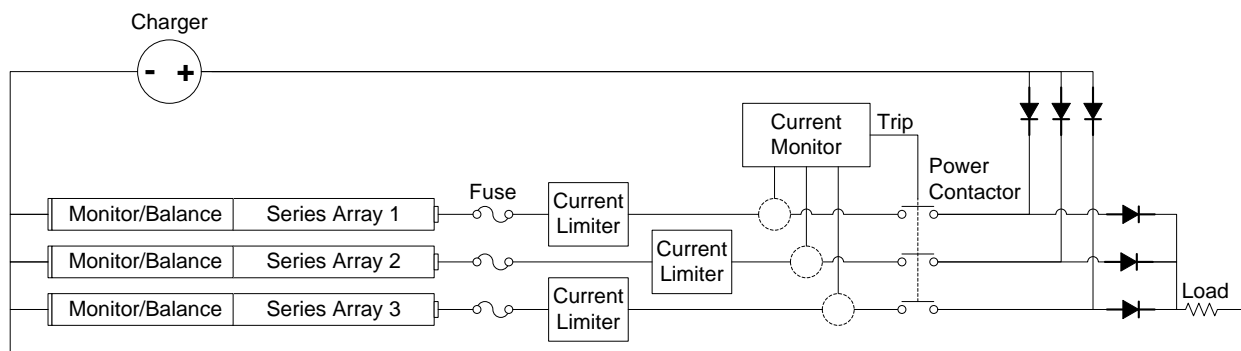


Figure 4-15. Battery module with one current monitor and power contactor.

4.1.3 Thermal Management

Thermal management is a very important aspect of module design, operation, and safety. The operating temperature of lithium batteries affects the life of the battery, the discharge rate, and available charge. Cells within a module must also be protected from extremes to prevent thermal runaway. Thermal management functions at the module level include, first, monitoring, then cooling, and, more specific to automotive applications, heating. This section introduces thermal management issues and techniques.

The module is ultimately integrated into a battery pack. The battery pack interfaces with the vehicle cooling system and passenger cooling system. Discussion of these aspects of thermal management is deferred to the battery pack discussion.

Though the need for cooling is more common, heating may be required for operation at low ambient temperatures. In some instances, cooling systems may be used for heating the battery module.

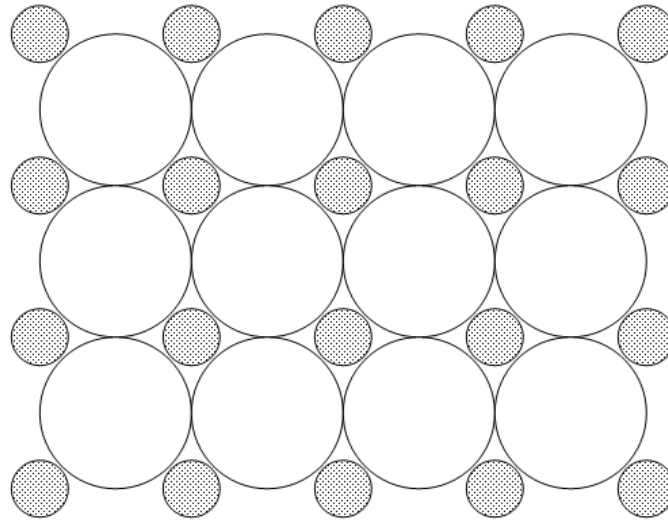
4.1.3.1 Heat Exchange System

The battery pack can have air, liquid, or refrigerant cooling. Liquid cooling media may be the traditional 50/50 water/ethylene glycol mixture or it may be part of a refrigerant cooling cycle. Cooling air can be outside air or cabin air, sometimes cooled by the air conditioning system, as in the Prius (Pesaran, Kim, & Keyser 2009).

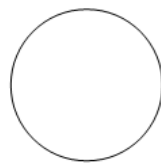
4.1.3.2 Conduction Matrix

A lithium battery module will be composed of many individual battery cells, which must be held at uniform temperatures. Heat must be conducted away from the cell matrix to a heat exchange mechanism. The cell type and cell configuration drive the conduction matrix design. Notional examples for cylindrical, pouch, and prismatic cells are shown in Figure 4-16 through Figure 4-19.

In the instance of cylindrical cells in Figure 4-16, tubes filled with heat exchange liquid are in the gaps between the cells. Figure 4-17 shows how solid fins can be located along the edges of pouch-type cells to conduct the heat to a cooling medium. Cooling is similar for both prismatic cells (Figure 4-18) and for an array (Figure 4-19).



Key



Cylindrical Battery
Array (End View)



Heat Matrix Array
(Cooling Tube)

Figure 4-16. Cylindrical battery array with liquid cooling tubes.

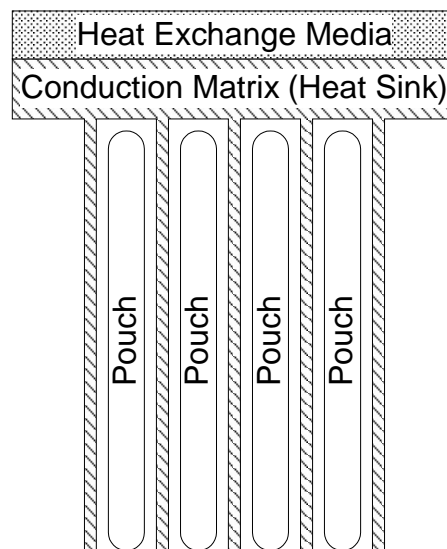


Figure 4-17. Pouch battery array with a heat sink conduction matrix.

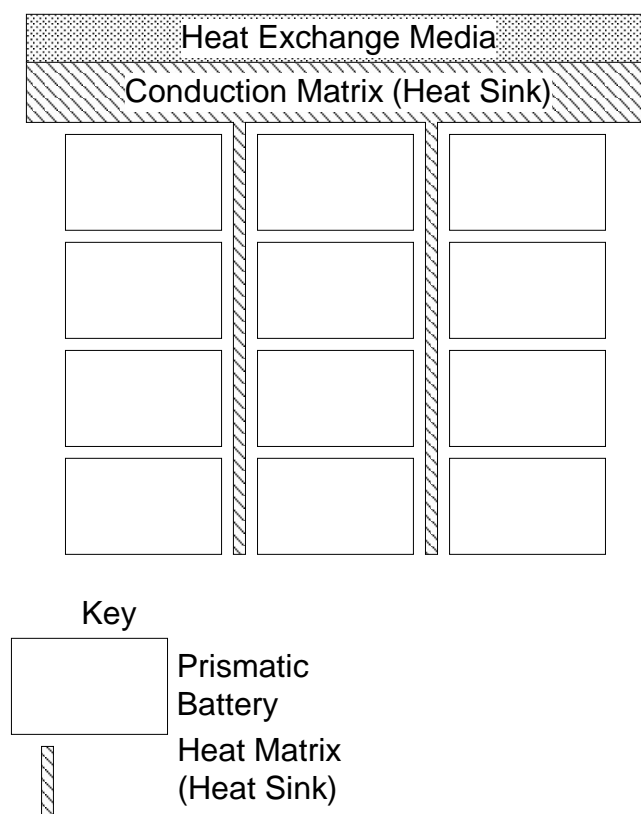


Figure 4-18. Prismatic battery array with a heat sink conduction matrix.

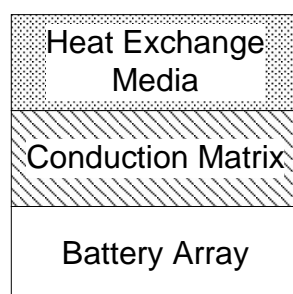


Figure 4-19. Generalized conduction in a model of a heat exchanger with a matrix.

Another method, described by Manning (2007), is the use of large terminals for conducting the heat out of the cell. In this case the heat sink (or fins) can be fitted to the terminals and cell interconnect. Ener1 (EnerDel) builds such prismatic cells and GAIA (Germany) builds such cylindrical cells. Saft also has produced cylindrical cells with a hollow tube through the center of the cell for cooling.

4.1.3.3 Module Temperature Monitoring

Module temperatures may be monitored at a number of locations including all or selected cells, heat exchanger inlet and outlet, and other locations. The temperature can be reported to the battery pack, or the module's own control electronics can disconnect the module from the load if the control system detects a thermal management problem.

A conceptual module with one temperature sensor per cell is shown in Figure 4-20. Depending on the conduction matrix, there may be a number of heat exchange media inlet and outlet temperature sensors. The control electronics within a module may also be connected to the conduction matrix and may have additional temperature sensors. A generalized thermal management model is shown in Figure 4-21. The heavy dashed line represents a thermal conductor from the control electronics to the conduction matrix to cool electronic components. The system model in Figure 4-22 shows the components for current protection as well as thermal management.

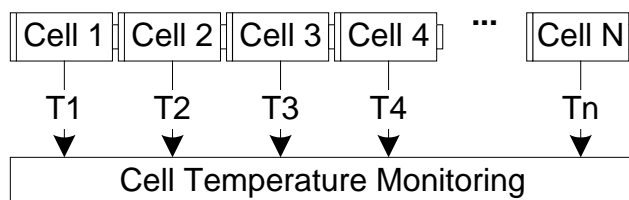


Figure 4-20. A module with one temperature sensor per cell.

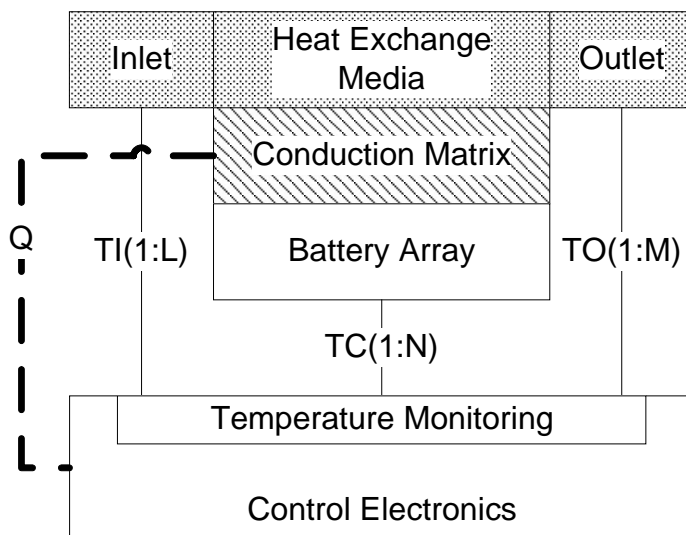


Figure 4-21. Generalized temperature sensor model.

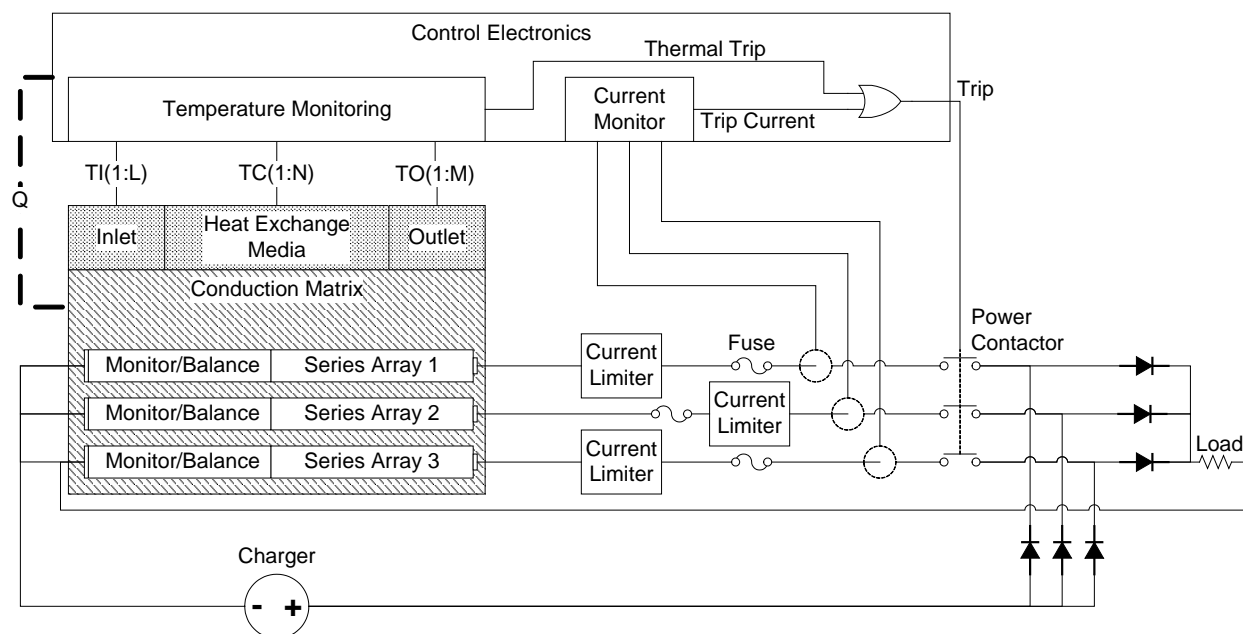
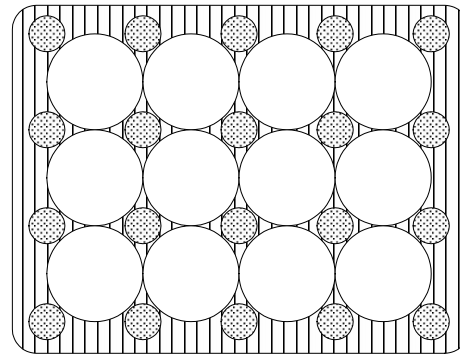


Figure 4-22. System model with both current management and thermal management.

4.1.3.4 Passive Phase Change Materials

Solid-to-liquid phase change materials have been proposed for thermal management. Typically a graphite matrix is filled with a phase change material (e.g., paraffin) and the battery packs are placed within the matrix. This design has been shown to absorb all the required heat at full discharge to maintain the battery packs at a safe temperature range. A major advantage of this design is that the heat generated during discharge, which is stored as latent heat in the phase change material, is transferred to the modules during relaxation periods and can maintain the temperature of the modules above the surrounding temperature for a long time. Thus the system can be used in a heating mode after some period of use. It is argued that the passive control provided by the phase change material may make active control a complementary or secondary function and may lead to simpler control designs. The concept is shown in Figure 4-23. The voids between the cylindrical cells and cooling tubes are filled with a material that melts (i.e., it changes from its solid phase to a liquid phase) at a temperature below the thermal runaway temperature of the cells. A related system (Kim, Gonder, Lustbader, & Pesaran, 2007) embedded the batteries in a graphite matrix phase change material. Analysis, experiments, and driving tests showed that phase change materials provided thermal management over short drives, but convective cooling was also needed in longer drives. Some consideration was also given to dissipating thermal runaway with the phase change material system. Change-of-phase material has been added to the overall system model in Figure 4-24.



Key

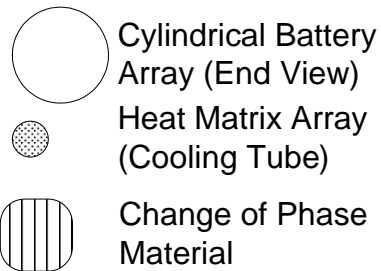


Figure 4-23. Cylindrical batteries with cooling tubes and change of phase material.

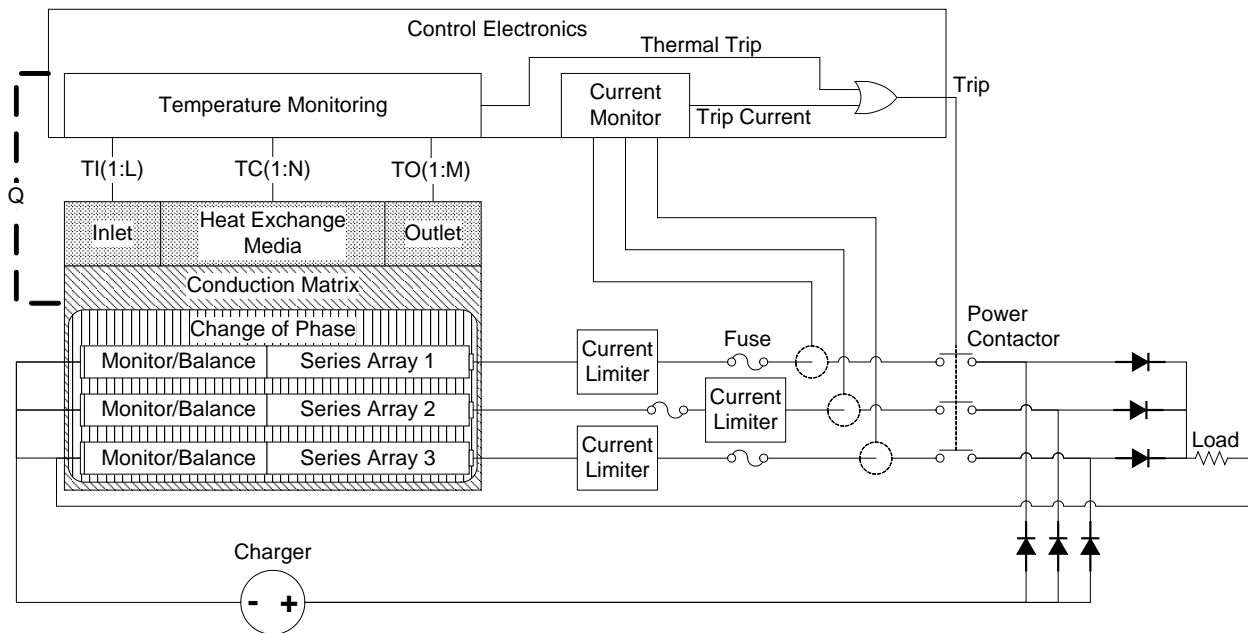


Figure 4-24. Module model with change of phase material added around the series arrays.

4.1.4 Other Safety Considerations

Other features may also be included in the design of a battery module such as interlock circuits, pressure sensors, and communication architecture that allows the battery status to be monitored by the automobile electronic control unit. The application and functionality of these features are discussed in this section.

Module designs must also include appropriate sizing of power cables, low resistance connections, electrical insulation, and the battery cell attachment mechanisms for safe, reliable operation in the event of a crash. Other safety measures such as hazard markings and uniquely keyed tooling and maintenance seals may be included in the module to deter unauthorized access.

The details of these requirements are not illustrated but are noted for completeness.

4.1.4.1 Interlock

An interlock signal from the battery pack to battery modules can be used to disconnect the module from the pack's high-voltage circuit. This type of signal may be used in a daisy chain manner, where one module passes the interlock signal to the next module until the interlock signal completes its path through the system.

An “Interlock In” and “Interlock Out” signal, a “Safe On” AND gate, and another pole on the power contactor have been added to the developing model diagram in Figure 4-25. The diagram indicates an interlock and power contactor included in both the module and the battery pack.

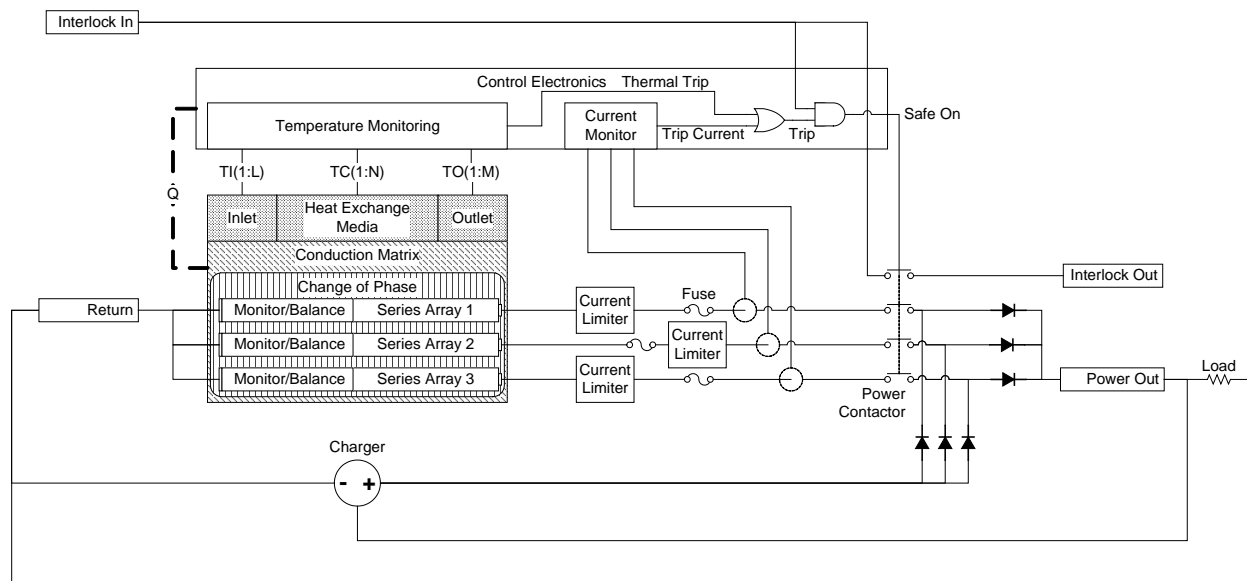


Figure 4-25. Module model with Interlock design elements.

4.1.4.2 Pressure Detection

An overheated lithium battery cell can release gas, leading to cell packaging rupture and cell failure. Depending on module and pack requirements allocation, the module, pack, or both may include pressure. Cells may include vents or pressure disks to provide a controlled means for out-gassing possible preventing adjacent cells from rupture, as illustrated in Figure 3-2 above. Unless otherwise stated in this analysis, the module design will include at least one pressure sensor.

A pressure sensor is shown to the right of the conduction matrix in the module model in Figure 4-26.

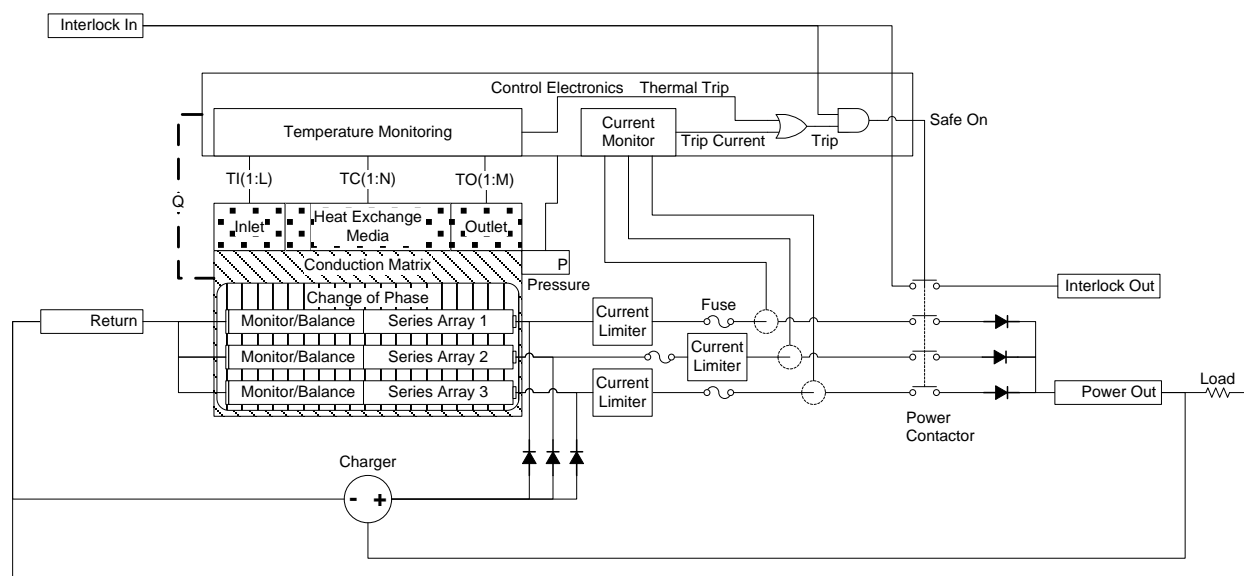


Figure 4-26. Module model with a pressure sensor.

4.1.4.3 Communication, Control, and Reporting

Lithium battery modules can be quite complex. They may include thousands of cells. Voltage and temperature measurements may be made for each cell. Module current, pressure, and coolant temperature measurements may also be made. The module calculates SOC and SOH based on these measurements. The module will also communicate with other modules or the battery pack controller to report critical data items such as SOH, SOC, and on/off status or respond to on/off commands. A battery module control electronics block diagram is shown in Figure 4-27.

A power supply converting high-voltage battery power to logic-level power needed to operate the controller and other module control electronics is needed. This diagram places that power supply within a control electronics assembly.

At the center of the diagram is a controller, most likely an embedded microprocessor. The controller is shown with supporting components such as a “watch dog timer” and power monitor. These supporting components help ensure that the controller remain operational and can recover from upsets.

Shown on the left side of the diagram are signal conditioning circuits and an analog-to-digital converter for module temperature, voltage, and pressure sensors. These circuits allow the controller to gather parametric module performance data. Controller algorithms calculate SOC and SOH from these parameters.

A buffer converts a Interlock In signal to logic levels and another buffer converts the Interlock In signal level to a Safe On signal. The Safe on signal is the logical combination of Temperature Trip, Over Current Trip, and Interlock signals used to turn the module output on and off. The interlock signal is passed through to connect-to-signal contacts in a relay to pass the interlock signal to the next circuit in the battery system interlock. As a default on power up, the controller should not assert Safe On until a full assessment of the SOH and interlock signals has been made.

The diagram shows a simple buffered Fail/Status signal and a controller-area network (CAN) bus for communicating module status to the battery pack. The status signal could be used to drive a simple status lamp for maintainer use. The CAN bus can receive and send data. The pack may command the module to turn on or off (set the Safe On signal on or off). The controller can also report Interlock In state, Safe On state, voltages, currents, temperatures, pressure, SOC, and SOH to the pack via the CAN bus.

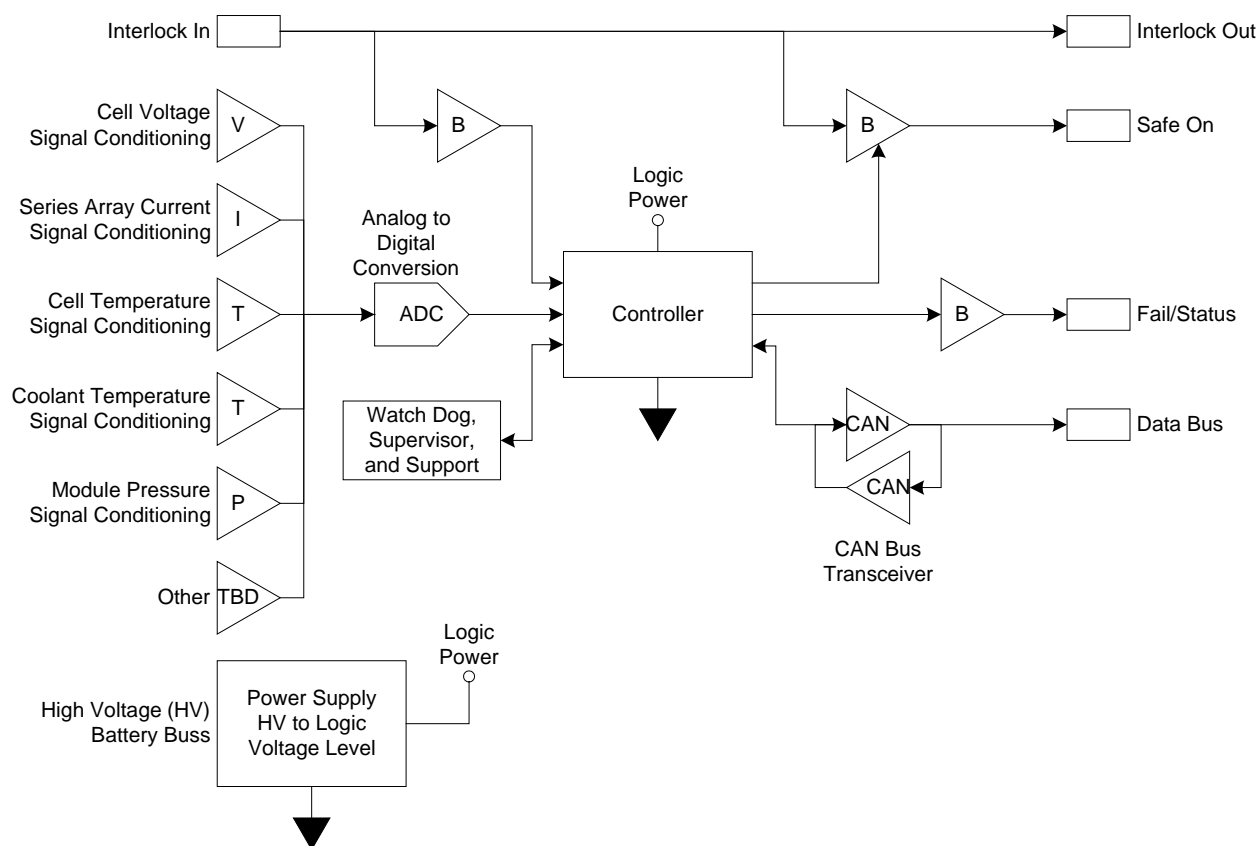


Figure 4-27. Module control electronic block diagram elements.

4.1.5 Battery Module Conclusion

The battery module is a complex system. The model presented in this discussion has grown from a simple string of battery cells to a complex system with many components and functions. When it is necessary to look at the detailed module functions, Figure 4-26 and Figure 4-27 should be used. However, the detail provided in these figures may not be necessary for all analyses. A more compact model is shown in Figure 4-28. This model shows input on the left side, module components in the center, and outputs on the right side. The CAN bus data items are further highlighted to the right of the outputs. An even more compact model is shown in Figure 4-29. These compact models may be used throughout this analysis.

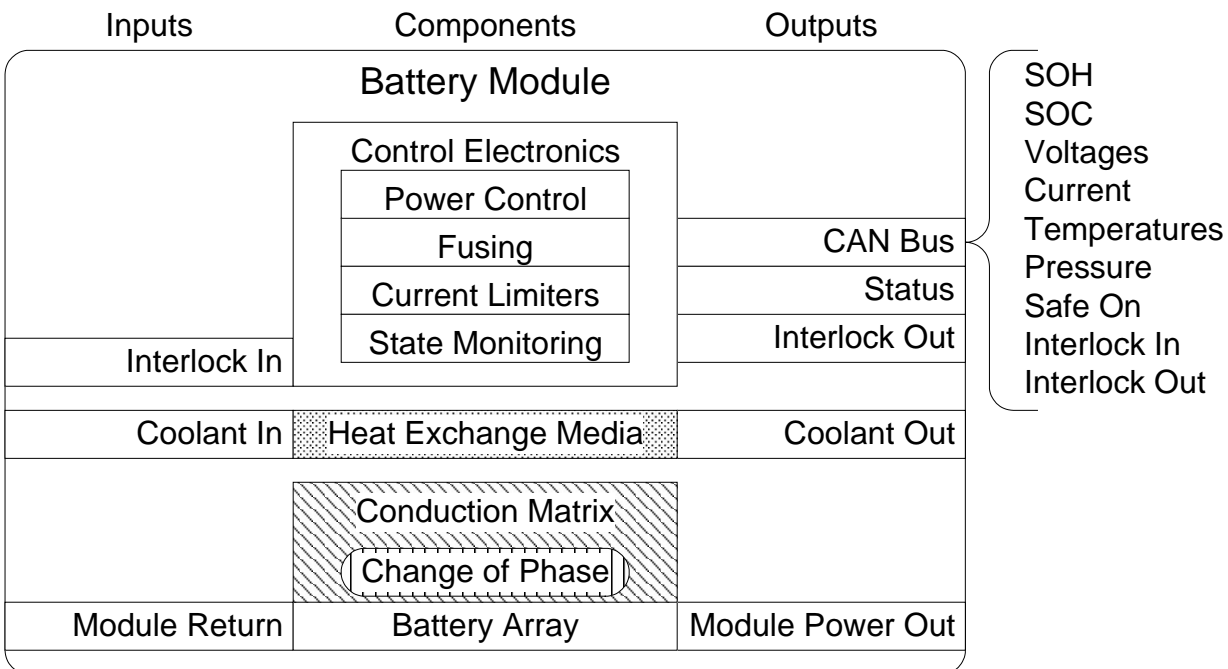


Figure 4-28. A complete model of a battery module.

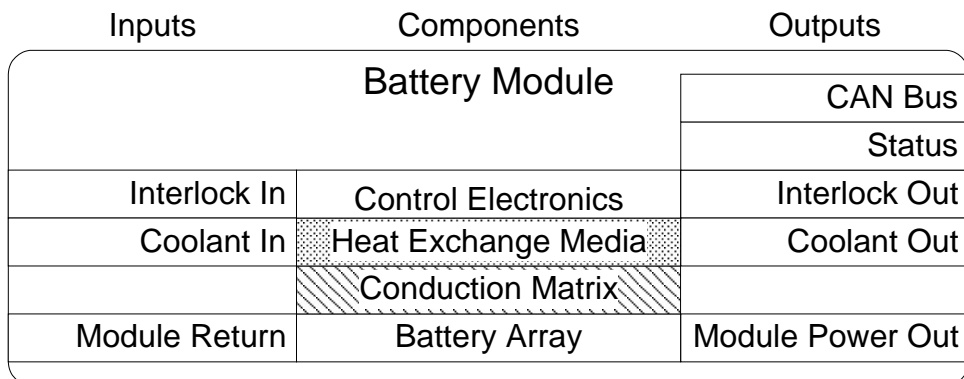


Figure 4-29. A compact model of a battery module.

4.2 Battery Packs

Battery packs integrate modules and other control, structure, and safety design elements into a complete vehicle power system. The pack interfaces to vehicle control systems to report its status, and it mounts to the vehicle structure. This section describes pack composition, details pack operation and control, and provides a general battery pack model.

4.2.1 Pack-Module Boundary

If battery modules can be thought of as large integrated batteries, then in some respects a battery pack is similar in nature to a battery module. Both pack and modules provide electrical power, require thermal management, and provide a measure of control.

4.2.2 Module Arrays

Like cell arrays in a module, battery packs include arrays of modules. Each module has positive and negative power connections. Those module connections must be attached in some manner within a pack. Again series, parallel, and series-parallel options exist. If the output voltage of the module is the rated pack voltage, then a parallel array of modules would be appropriate. A parallel array of modules is illustrated in Figure 4-30. The Tesla Roadster battery pack is configured in a series array of 11 modules: each module is configured with a series array of nine “bricks,” and each brick is a parallel array of 69 cells (Tesla, 2013). The Chevrolet Volt battery pack is built up from groups of three cells connected in parallel, and 96 of these groups are connected in series for a total of 288 cells which produce 360V. These 288 cells are packaged in nine modules, two 18-cell modules and seven 36-cell modules (DeMeis, 2012; Abuelsamid, 2010; Wikipedia, 2013).

The PASC module configuration included parallel blocking diodes and battery recharging diodes. A parallel array of modules may not need similar diodes because the diodes already exist at the module. Adding parallel blocking diodes protects modules from other module failures within an array. Recharging diodes are needed to permit recharging from the motor/generator/alternating current (AC) to direct current (DC) converter, wall charger, or any other recharging component on the high-voltage bus. The parallel blocking diodes also provide reverse polarity protection for the modules. Unless stated otherwise the pack model in Figure 4-31 with parallel blocking diodes and recharging diodes will be used in the remainder of this analysis.

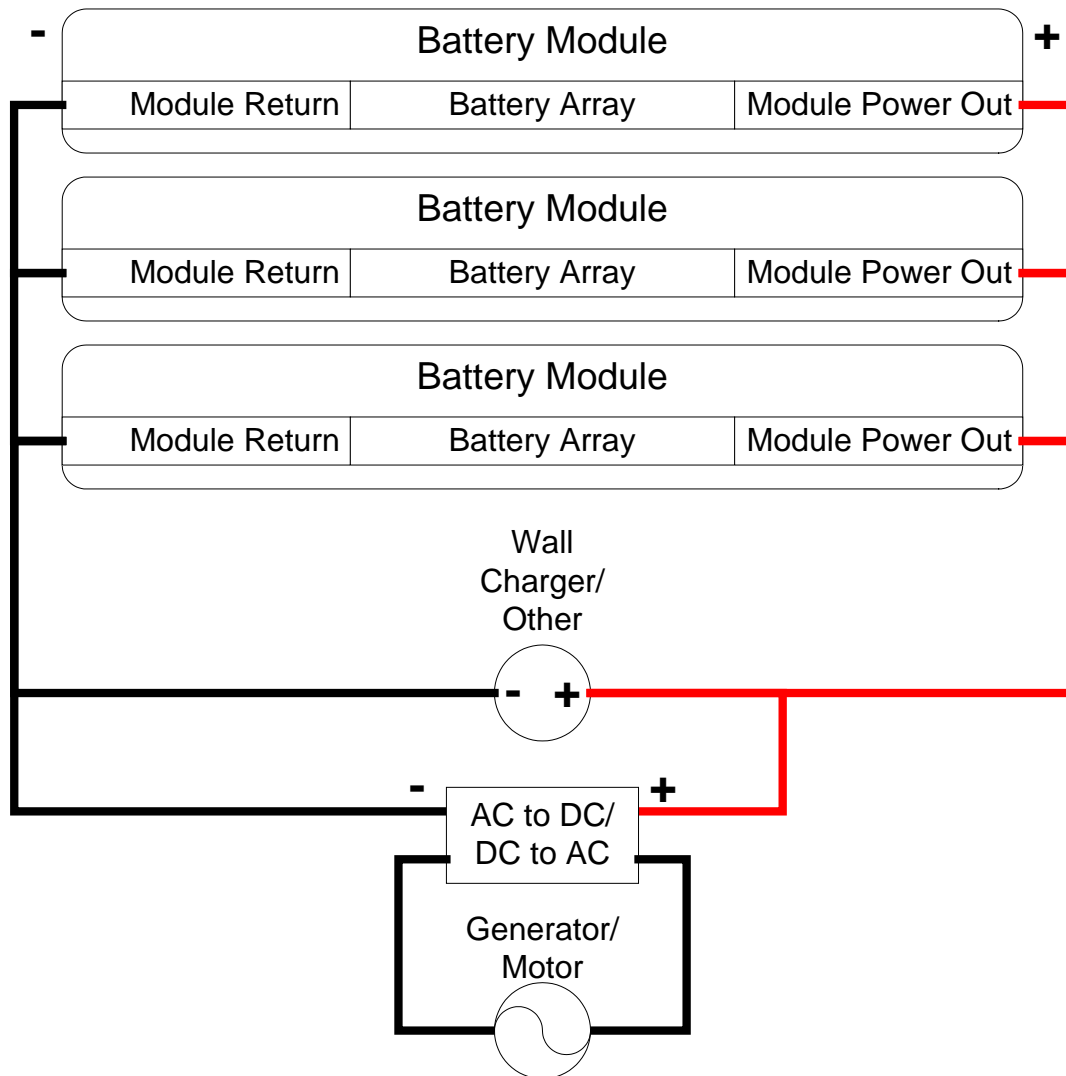


Figure 4-30. Parallel array of modules with a motor-generator and wall charger.

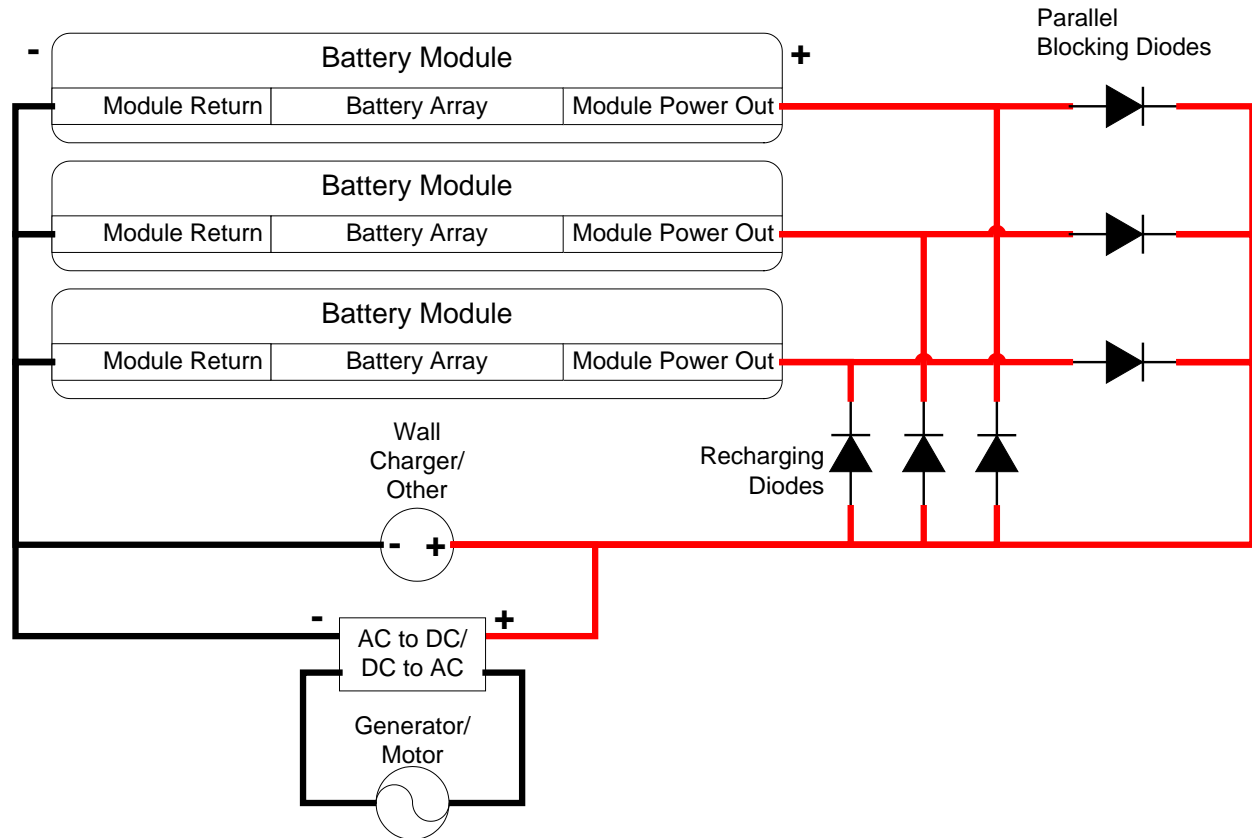


Figure 4-31. Parallel array of modules with motor/generator, wall charger and diodes.

4.2.3 Pack Power Contactors and Interlock Control

Pack interlock and power contactors are controlled by pack control electronics as shown in Figure 4-32. The vehicle provides an interlock signal indicating that the vehicle system grants the battery permission to turn on its output power. Pack control electronics qualifies the interlock signal and starts an interlock daisy chain. The daisy chain passes through all of the modules and terminates at a power contactor signal terminal. A “Safe On” signal from the pack control electronics controls the power contactor, connecting the pack high-voltage bus to the vehicle high-voltage bus and finally passing the interlock signal back to the vehicle control systems.

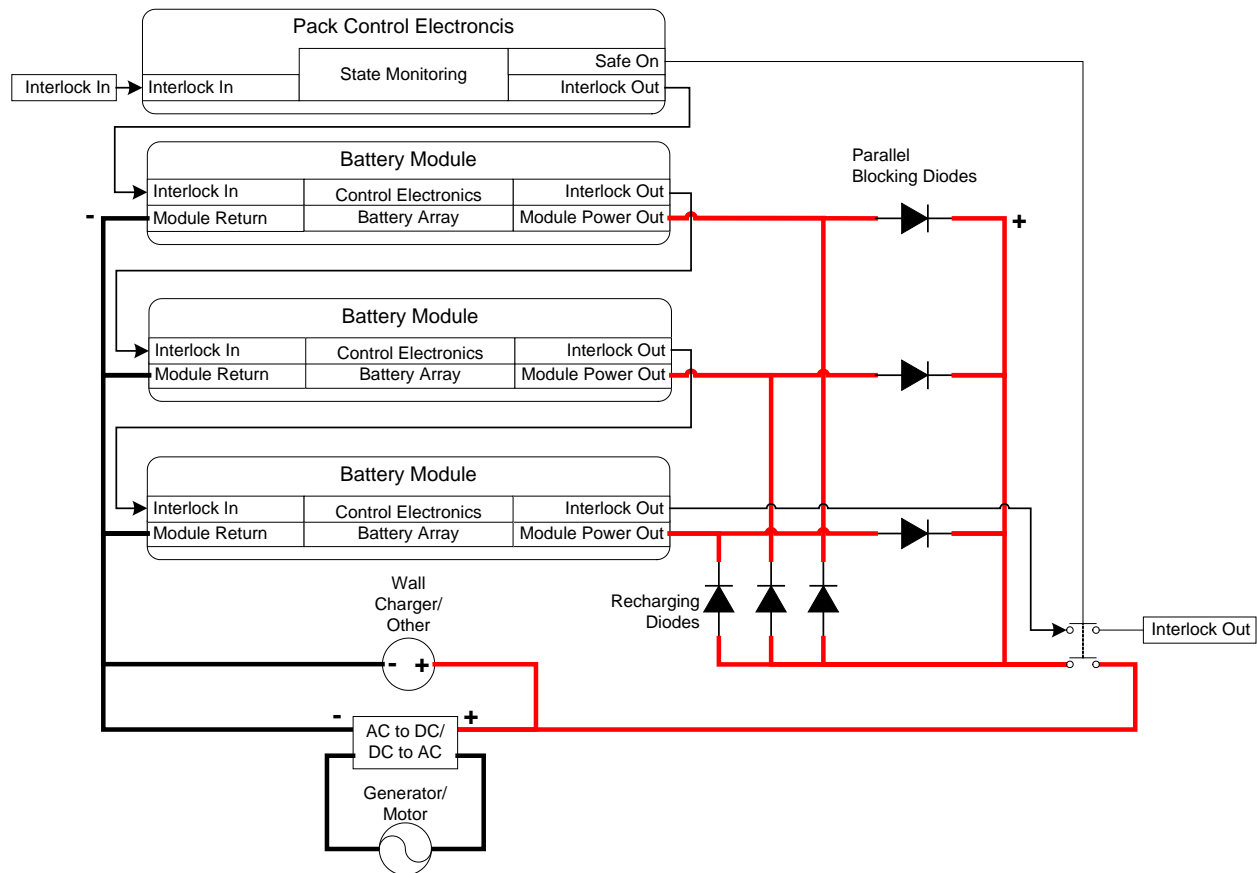


Figure 4-32. Pack control electronics qualifies the vehicle interlock and enables the output power contactor.

4.2.4 Thermal Management

There are numerous heat transfer approaches to designing a battery thermal management system. The ultimate design goal is maintaining the battery pack at an average temperature within the battery's specifications, and with even temperature distribution throughout the pack. The control variables may be air or liquid flow rates, depending upon the cooling system, or heater input. Some passive and active control design concepts follow from the work of Pesaran (2001). However, we note that the charging/discharging controllers should also be considered part of the thermal management system, since their operation determines the rate of heat generation. Table 4-1 lists prevailing heat transfer methods and their characteristics.

Table 4-1. Heat transfer methods for Li-ion battery thermal control.

Description	Heat Transfer Mechanism	Modes	Control Variables
Passive Cooling (Air)	Outside air for cooling and ventilation Requires mild ambient temperatures of 10°C to 35°C	Cooling only	Speed of fan used to draw outside air
Passive Heating and Cooling (Air)	Internal cabin air for heating, cooling, and ventilation	Cooling and heating Dependent on temperature of cabin air	Speed of fan used to draw cabin air
Active Heating and Cooling	Outside air for heating, cooling, and ventilation Includes auxiliary heater and/or evaporator	Cooling and heating	Speed of fan used to draw outside air Auxiliary heater input Evaporator cooling input
Passive Cooling (Liquid)	Heat exchanger between liquid heat transfer medium and outside air for cooling Pump to circulate liquid and fan to force outside air through heat exchanger	Cooling only	Speed of fan used to draw outside air Flow rate of pump to circulate fluid
Active Moderate Cooling and Heating (Liquid)	Heat exchanger between liquid heat transfer medium and vehicle engine coolant for heating and cooling Two pumps: (a) to circulate liquid through battery pack and (b) to force engine coolant through heat exchanger.	Moderate cooling and heating	Flow rates of pumps used to circulate working fluids
Active Cooling and Heating (Liquid)	Two heat exchangers: (a) between liquid heat transfer medium and vehicle engine coolant and (b) between liquid medium and air from evaporator or refrigerant from condenser Two pumps: (a) to circulate liquid through battery pack and (b) to force engine coolant through heat exchanger.	Moderate cooling and heating	Flow rates of pumps

Liquid coolant is assumed for Figure 4-33. The model shows temperature sensors at both the inlet and outlet manifold, allowing the pack control electronics to estimate the heat generated by the modules. Additionally module temperature data are transmitted to the pack control electronics via the CAN bus.

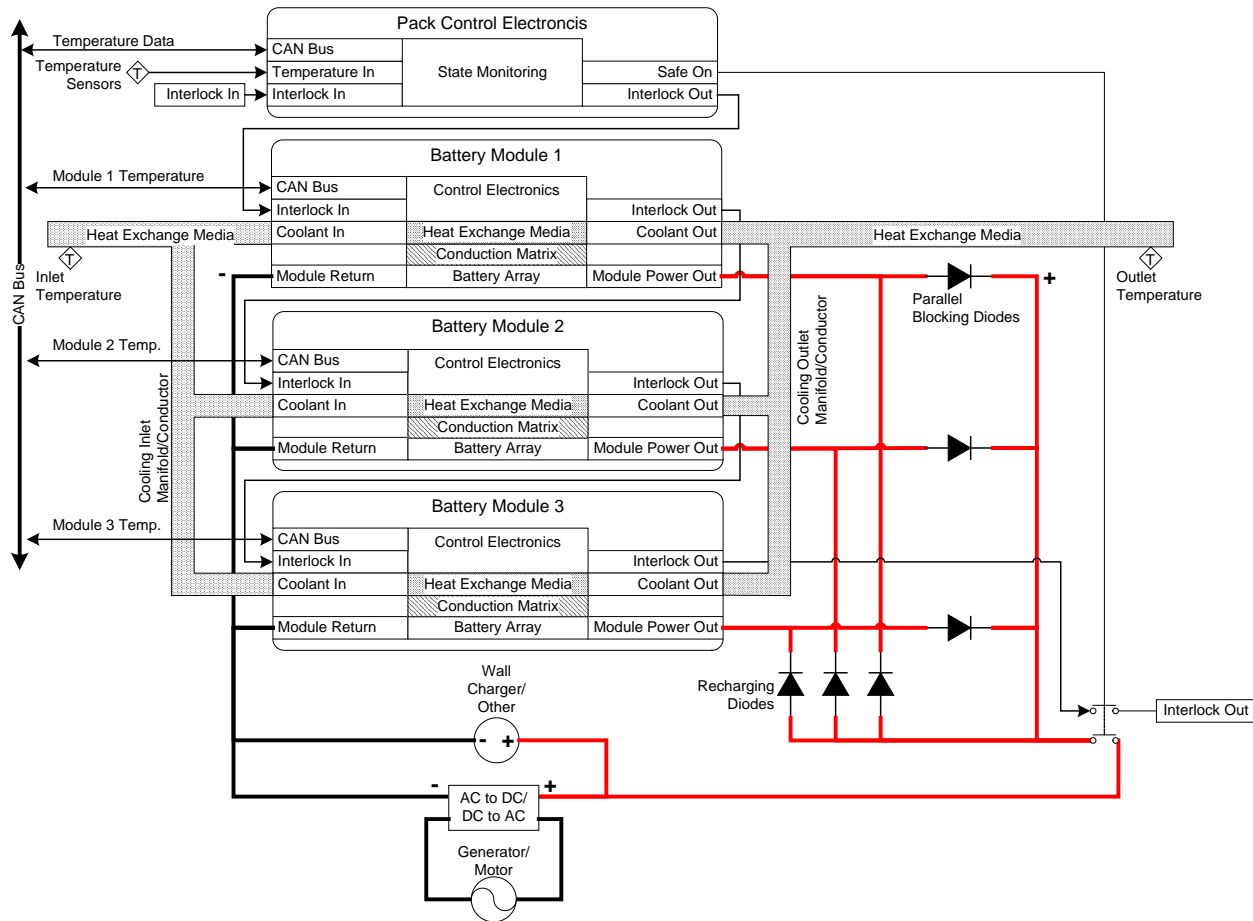


Figure 4-33. Pack inlet and outlet manifolds distribute heat exchange media to modules.

4.2.5 Current Limiting – Fusing

Current limiting at the pack level in the model is accomplished with an electrical fuse and by current monitoring and power contactor control. A fuse is connected in series with the power contactor. In the event that an overcurrent event or short circuit occurs, the fuse will open, protecting the pack from an overcurrent exception.

In the model shown in Figure 4-34, a current sensor is connected in series with the power contactor. The output on the current sensor is monitored by the pack control electronics. When a current spike of sufficient magnitude and duration is detected, an Overcurrent Trip condition is detected. The Overcurrent Trip is a signal that disconnects the pack high-voltage bus from the vehicle high-voltage bus at the power contactor. Though both fuse and current monitoring and control methods are used in the model, the current monitoring and control method was selected for this design due to its simplicity and potentially lower maintenance requirements. The fuse provides a simple, reliable backup method that cannot fail due to software, sensor, or controller failure.

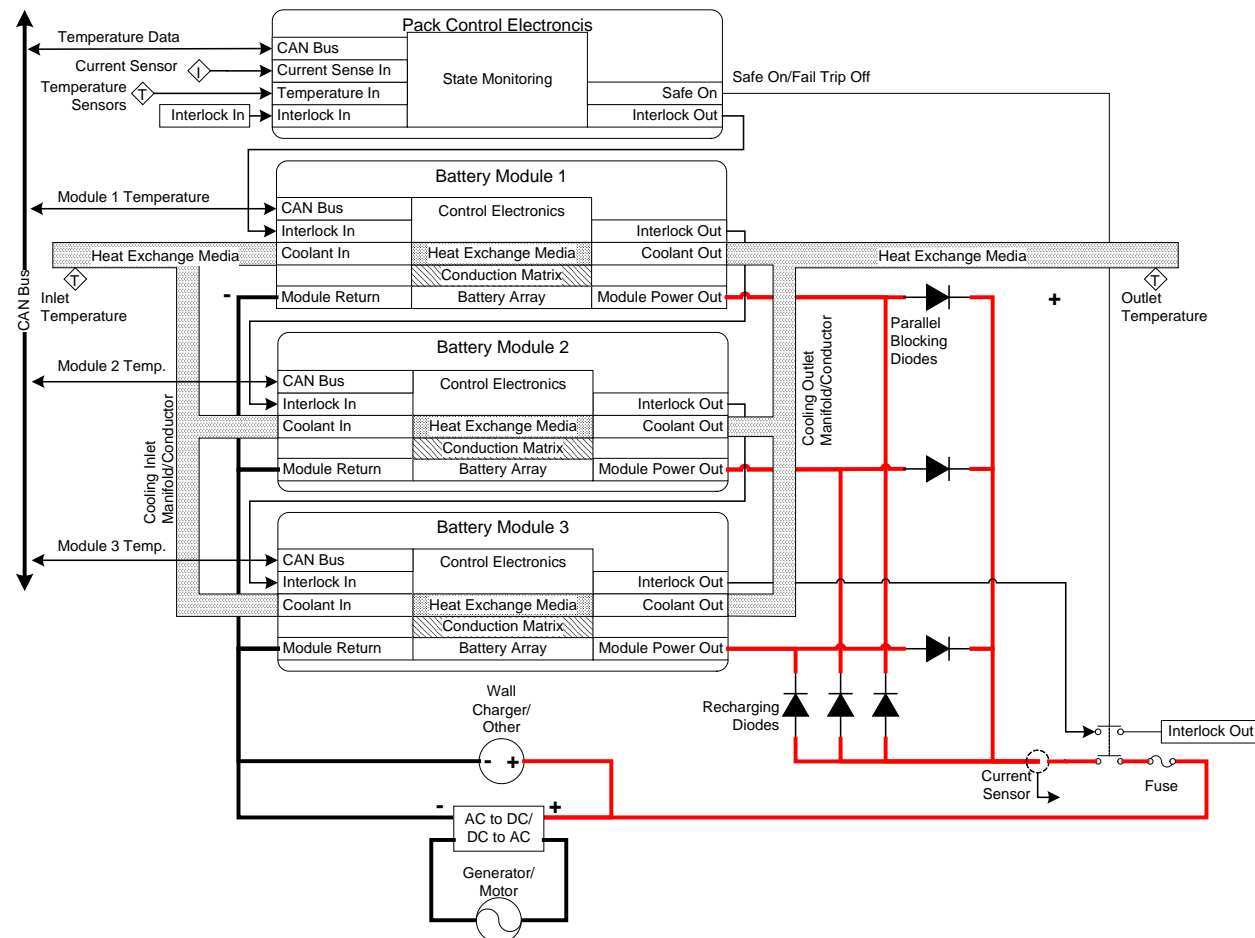


Figure 4-34. Fuse and current monitoring and power contactor control protect the module from over current events.

4.2.6 Additional Battery Pack System Safety Features

In addition to the design features included in the model thus far, other pack safety features are included in this model: crash detection, rollover detection, pressure sensors, and smoke detection sensor.

Modern vehicles include crash detection for deployment of airbags and possibly other safety features. When the vehicle detects a crash, the model assumes that the vehicle control system will negate or turn off the battery interlock thus disconnecting the pack from the vehicle high-voltage bus. Adding a crash sensor within the pack provides an additional layer of safety; the Tesla is known to do so. Two crash sensor circuits must fail before the disconnect function can fail.

Crash sensors can be designed from micro-electromechanical systems accelerometers. These accelerometers are small electrical chips, and they are typically configured for sensitivity in three axes: longitudinal, lateral, and vertical. These sensors can also detect a rollover event. When either event is detected, the battery pack Safe On/ Fail Trip Off signal is asserted in the Fail Trip Off state, disconnecting the pack from the vehicle high-voltage bus.

In addition to the pressure sensors included in the module model, the pack model also includes pressure sensors. The sensors detect module to module pressure. When a threshold is exceeded, the Safe On/Fail Trip Off signal is set to the Fail Trip Off state, disconnecting the pack from the vehicle high-voltage bus.

A smoke detector is included to detect fires, potential fires, or other gases. When the detector senses a smoke or gas event, the Safe On/Fail Trip Off signal is set to the Fail Trip Off state, disconnecting the pack from the vehicle high-voltage bus. These additional sensors are shown in Figure 4-35.

Similar to those used in modules, other safety measures such as hazard markings and uniquely keyed tooling and maintenance seals may be included in battery packs to deter unauthorized access. The details of these requirements are not shown in the sketches but are noted for completeness.

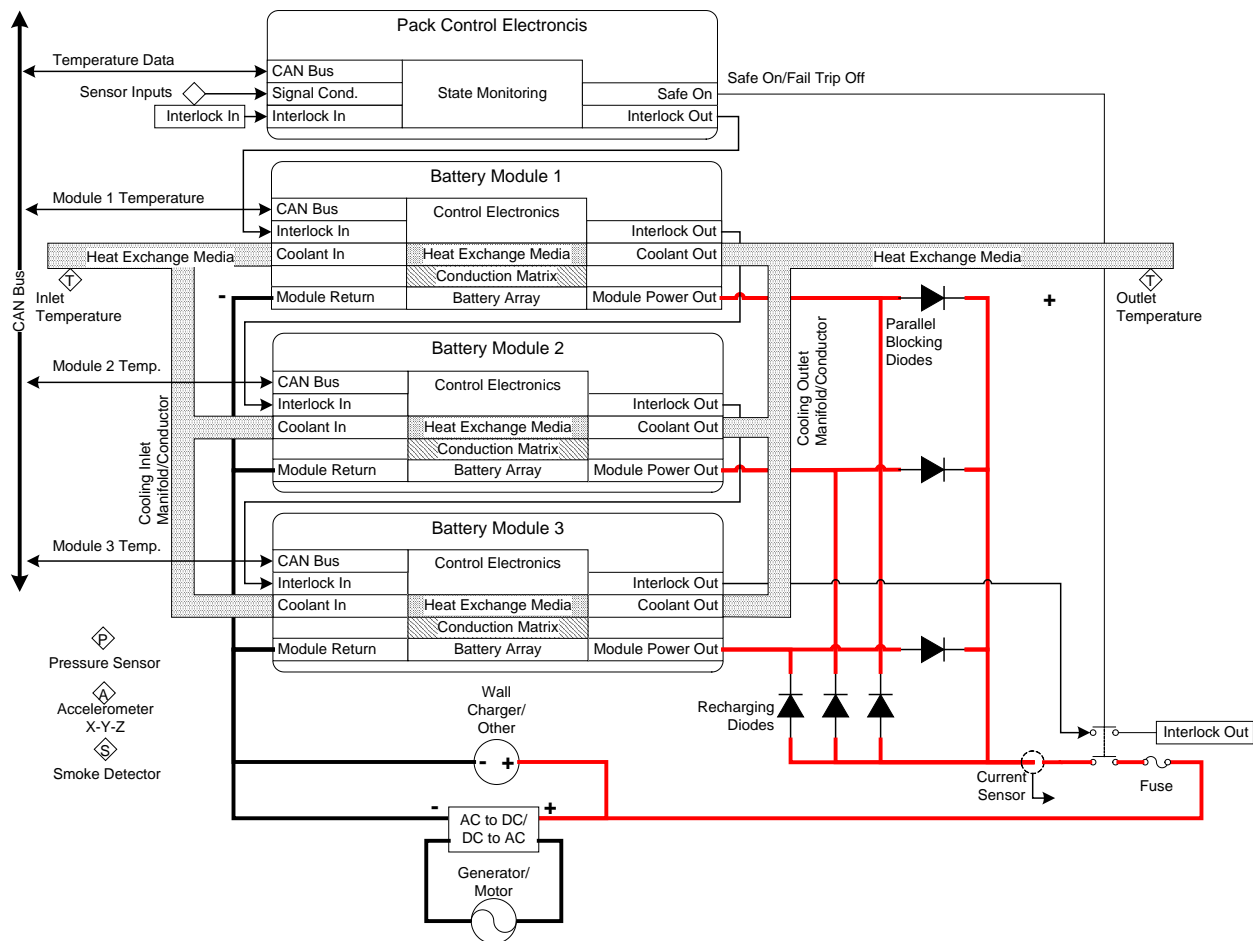


Figure 4-35. Pack safety sensors.

4.2.7 Communication, Control, and Reporting

Like battery modules, battery packs have communications, control, and reporting functions. The pack polls modules for SOH, SOC, voltages, current, temperatures, “Safe On” state, interlock state, and any other data. A model of the pack control electronics is shown in Figure 4-36.

A power supply converts high-voltage battery power to a low voltage for electronic control circuits. This diagram places that power supply within a pack control electronics assembly.

At the center of the diagram is a controller, most likely an embedded microprocessor. The controller is shown with supporting components such as a “watch dog timer” and power monitor. These supporting components help ensure that the controller remains operational and recovers from upsets.

On the left side of the diagram are signal conditioning circuits and an analog-to-digital converter for temperatures, voltage, current, pressure, smoke or fire detector, and crash detector. These circuits allow the controller to gather module performance data. Controller algorithms calculate SOC and SOH from these parameters. The crash sensor and smoke sensor are used to disconnect the pack high-voltage bus from the vehicle high-voltage bus when an event is detected.

A buffer converts an “Interlock In” signal to logic levels and another buffer converts the

“Interlock In” signal level to a “Safe On” signal. The “Safe On” signal is the logical combination of safety component activations including temperature, overcurrent, and interlock signals used to turn the module output on and off. The interlock signal is passed through to connect-to-signal contacts in a relay to pass the interlock signal to the next circuit in the battery system interlock. When the vehicle is started, the controller should not assert “Safe On” until a full assessment of the SOH and interlock signals has been made.

The diagram shows a simple buffered status signal and a CAN bus for communicating pack status to the vehicle control system. The status signal could be used to drive a simple status lamp for maintenance. The CAN bus receives and sends data. The vehicle may command the pack to turn on or off (set the Safe On signal on or off). The controller can also report internal information to the vehicle control system via the CAN bus.

Other controller features designed to manage the effects of electrostatic discharge (ESD), electromagnetic interference (EMI), lightning, alternator load dump, and other transient events are not shown in the diagram but are essential for reliable operation. The most fundamental circuit components for providing this type of protection are capacitors, varistors, diodes, and Zener diodes.

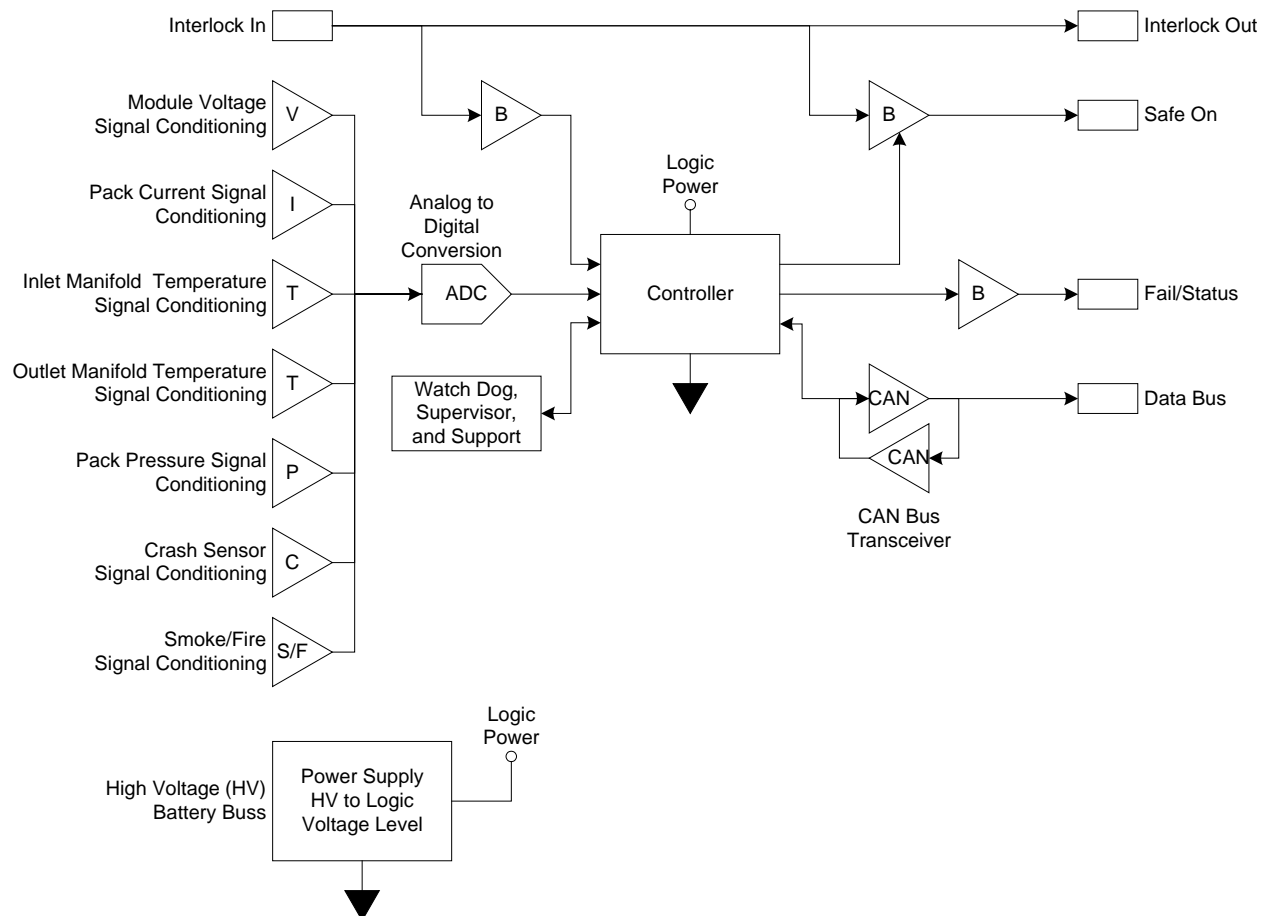


Figure 4-36. Pack control electronics block diagram.

4.2.8 Supercapacitors

Supercapacitors handle burst current better than batteries and might appear as a supplemental component in a battery pack to aid in meeting sudden acceleration demands or in powering small motors on the vehicle. Although they are not batteries and they are not based on lithium chemistry, they are included for completeness in considering a system. Supercapacitors, also known as ultracapacitors or double-layer capacitors, have a much greater surface area on their electrodes than conventional capacitors. Unlike conventional capacitors, they are filled with an electrolyte and have an insulator to separate the electrodes (Schindall, 2007).

Like batteries, supercapacitors are electrochemical components. Because of this electrochemical similarity, supercapacitors have a relatively low cell voltage of 2 to 3 volts, and so, like battery cells, must be connected in series to achieve high output voltages used in electric vehicles. In addition, supercapacitors are similar to batteries in that they generally require cell balancing circuitry to ensure that overcharging of one cell in series does not occur. A model of a supercapacitor array with charge and discharge diodes is shown in Figure 4-37 and a simplified version of the same circuit is shown in Figure 4-38. To achieve a rating of 300 V, each series array must be made of many individual supercapacitors. Connecting capacitors in series, however, reduces the total capacitance of the series array and a higher capacitance can only be achieved by connecting series arrays of supercapacitors in parallel as shown in Figure 4-39.

The advantages of supercapacitors over batteries include a very high number of charge/discharge cycles (hundreds of thousands to millions) and higher rates of charge and discharge current. Supercapacitors are therefore very good devices for capturing and returning energy from regenerative braking.

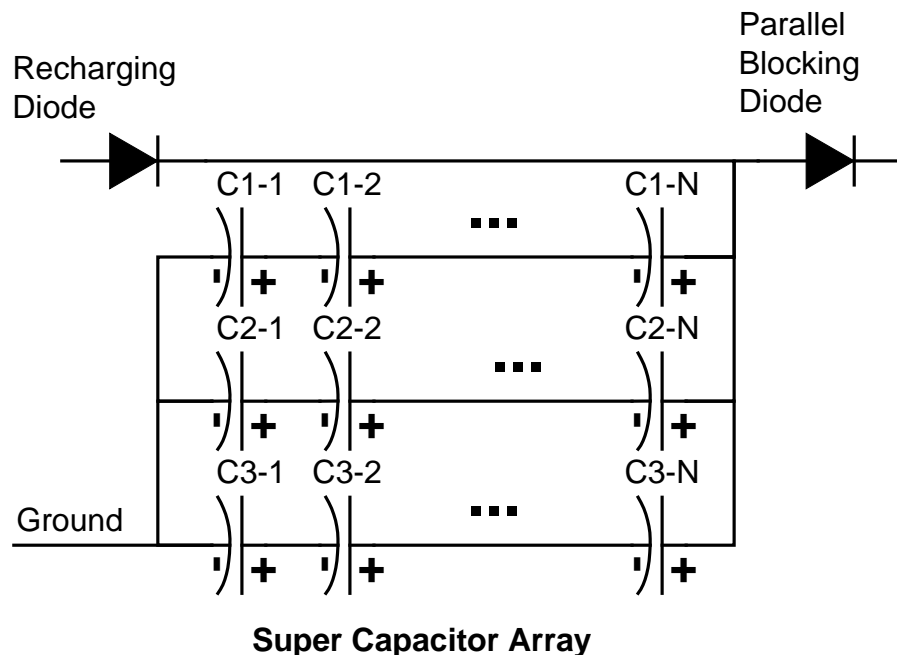


Figure 4-37. An M-by-N supercapacitor array with recharge and blocking diodes.

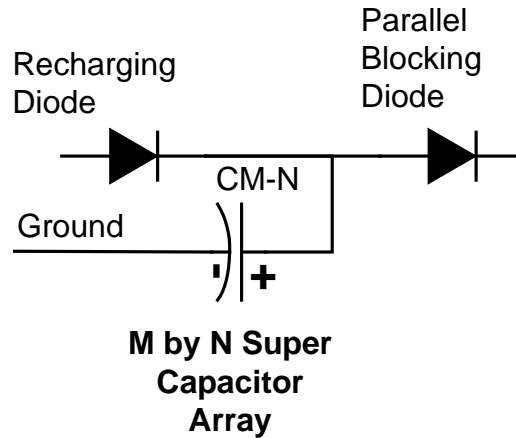


Figure 4-38. Simplified M by N supercapacitor array with recharge and blocking diodes.

The simple supercapacitor circuit shown in Figure 4-40 presents some system design challenges. At the application of power the supercapacitors look like a short circuit to ground. This characteristic presents a problem for charging sources. The capacitors cannot be directly connected across the batteries or generators without overloading those sources. A more sophisticated supercapacitor charge management system is required for use in vehicles.

A digital signal processor or microcontroller can be used to manage the supercapacitor rate of charge and discharge. When the vehicle signals a regenerative cycle, the DSP turns on the gate of a recharging field effect transistor. During a discharge cycle (an acceleration cycle), a voltage converter converts the stored charge to power at the vehicle high-voltage bus voltage. Controlling (turning on and off) charging during a brake or regeneration cycle prevents the capacitor from short circuiting the battery, generators, wall regeneration, or other power sources. Converting stored supercapacitor charge that has been stored at a lower voltage to a higher voltage for acceleration or slow recharge cycles reduces the number of capacitors in an array connected in series, thus increasing the total available capacitance. A conceptual circuit and simplified circuit of this circuit are shown in Figure 4-40 and Figure 4-41. A simplified pack model with supercapacitors and supercapacitor charge management is shown.

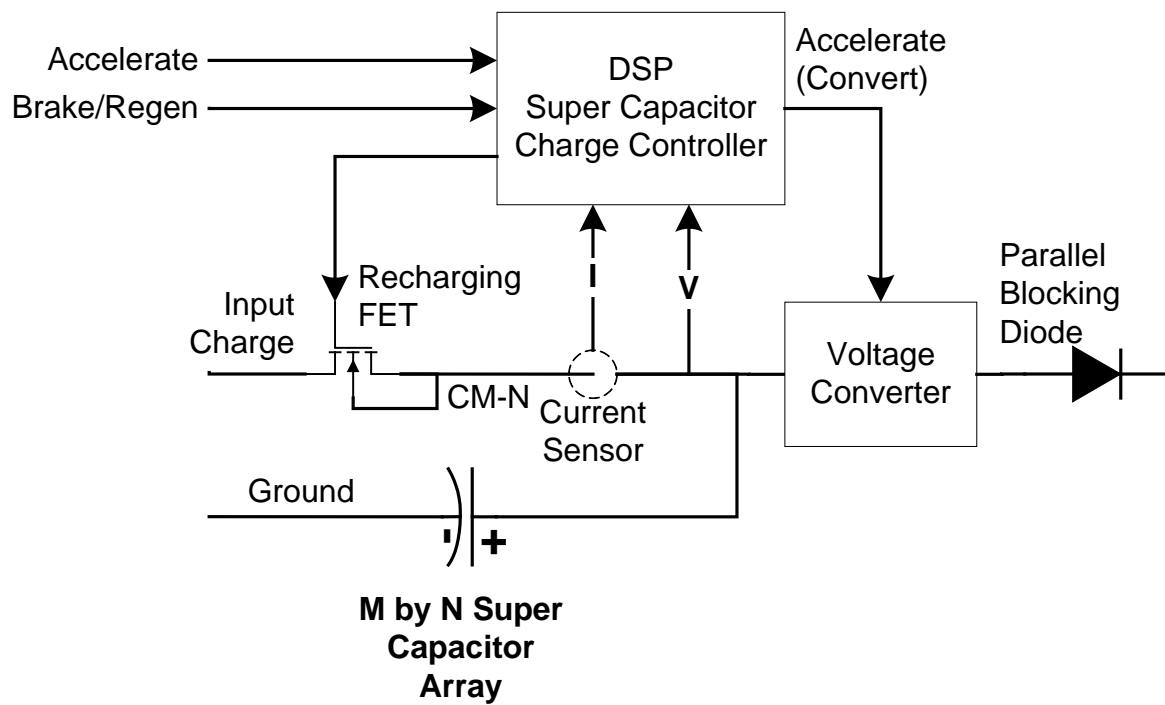


Figure 4-39. Supercapacitor array with recharge and discharge management.

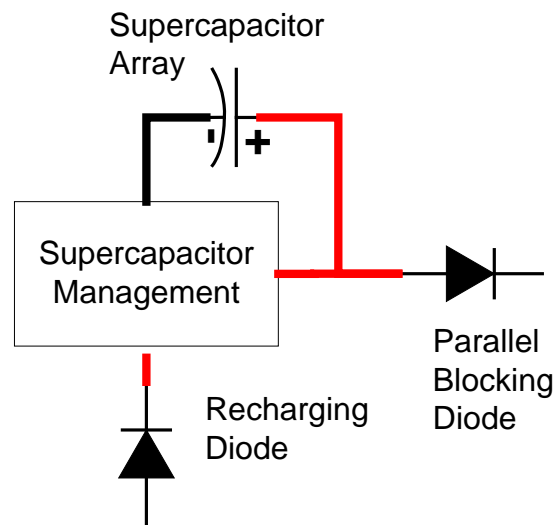


Figure 4-40. Simplified supercapacitor with charge and discharge management.

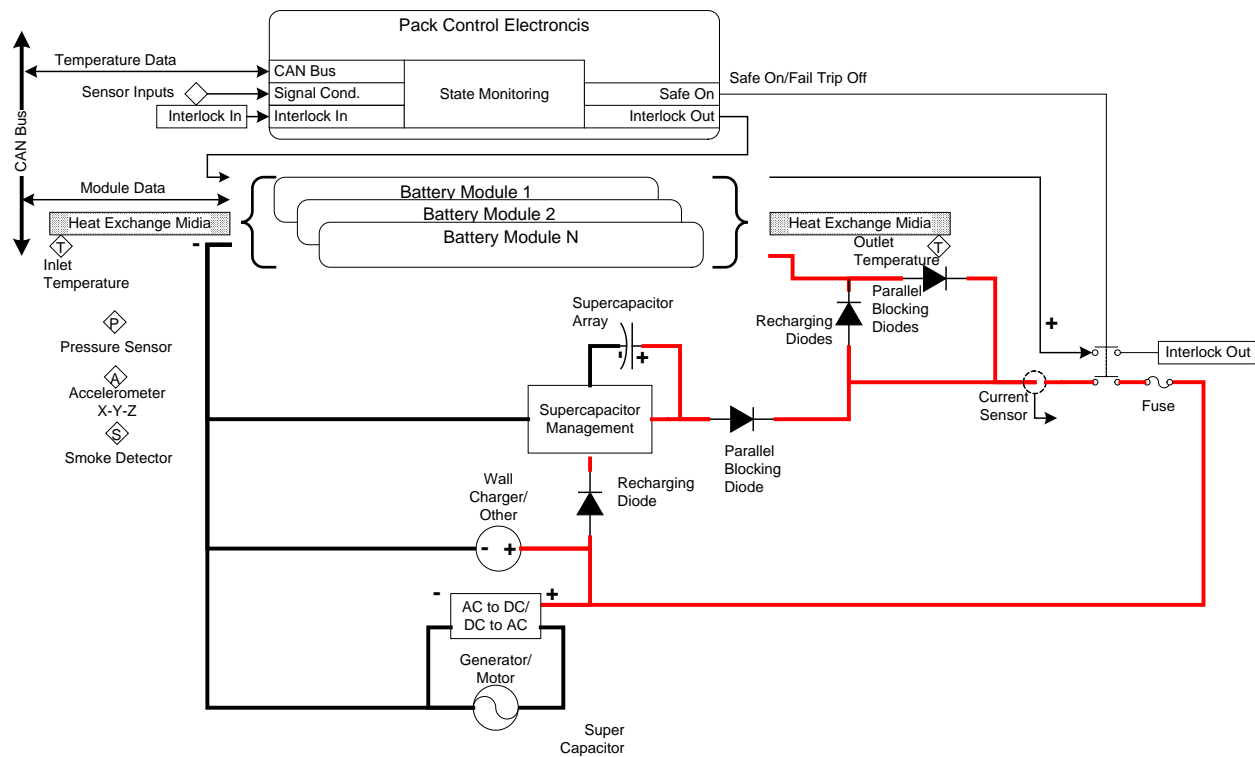


Figure 4-41. Simplified pack model with a supercapacitor array and supercapacitor charge management.

4.3 Integration With the Vehicle

Integration of lithium-chemistry battery packs adds to the increasing complexity of modern vehicles. All of the functions described above to provide for the safety of the battery must be supported, while meeting the vehicle's requirements for power and packaging. The pack must accept power from the internal combustion engine and generator, external plug, and/or regenerative braking, and it must supply traction power. Its size, weight, and location must be consistent with the vehicle's overall balance requirements for ride and handling, and its location must not degrade the vehicles' crashworthiness. The pack and its mountings must tolerate the shock and vibration load and the corrosion environment of the vehicle.

The pack structure includes the battery pack outer cover or skin, mechanical attachment points for battery modules, and mechanical attachment points for mounting the pack to the vehicle. The pack's structure must resist bending, crushing, foreign object penetration, and corrosion.

Electrical interconnection is required for battery power and return, communication through the CAN bus, and ground bonding for safety and electrical filtering. Electrical isolation and insulation are critical to the safe operation of the battery pack within a vehicle.

Specific parameters for the system structure and interconnection depend on implementation. The block diagram of Figure 4-42 illustrates these issues.

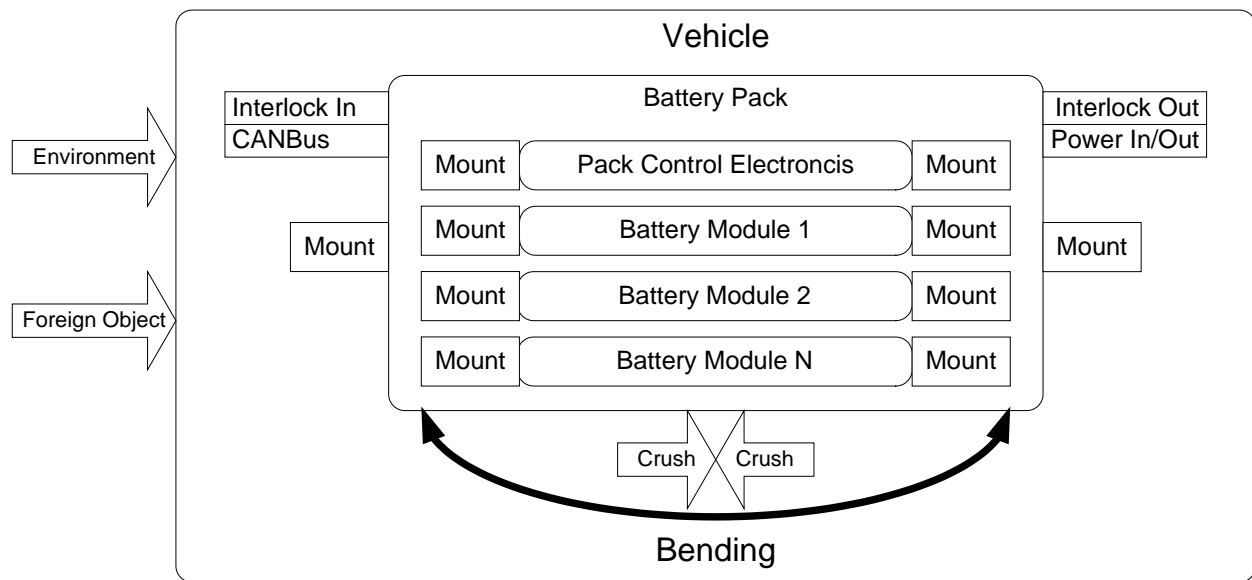


Figure 4-42. Battery pack structure block diagram.

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5 HEV, PHEV, and BEV Battery System Analysis

5.1 Introduction

Classes of vehicles with some electrical drive capability include BEVs (e.g., Tesla Roadster or Nissan Leaf), HEVs (e.g., Toyota Prius), and PHEVs (e.g., Chevy Volt). However, the HEV class can be further divided in to Micro HEV, Mild HEVs, and Strong (Full) HEVs. The array of vehicles and implementations are broad. In this section these systems will be introduced and compared, with a primary focus on battery and battery system safety.

5.2 HEVs

5.2.1 Micro HEVs

Micro HEVs are also referred to as Stop-Start HEVs. A Micro HEV improves fuel economy by turning off the ICE during vehicle stops and restarting the engine with pressure on the accelerator pedal, hence stop-start. This type of HEV provides modest fuel savings during stops with the least overall change to a traditional automobile architecture. Thus fuel is saved during stops, providing improved economy for heavy city driving. While stopped the battery and electrical system maintain power to electrical loads including instrumentation and control, lights, and comfort and entertainment. If stopped long enough, the engine may restart to recharge the battery. The battery in a Micro HEV is, or should be, larger than a traditional battery. The limited number of charge cycles of the familiar flooded lead-acid battery makes it a poor choice. A valve-regulated lead-acid (VRLA) battery provides more cycles and a longer life. Example Micro HEVs are the 2004-2005 Chevrolet and GMC Silverado and Sierra pickup trucks.

The electrical elements of the ICE are shown in Figure 5-1. A Micro HEV system is shown in Figure 5-2. The key differences between the ICE and Micro HEV systems are outlined in bold in Figure 5-2. They include a larger battery, larger alternator, and larger starter. The larger components are needed for more frequent engine starts and heavier recharging cycles.

In an ICE system, the brake and steering systems are traditionally hydraulic systems, with the hydraulic pump is powered by the ICE. In a Micro or other HEV system, hydraulic power is lost when the engine is turned off, which would result in a loss of hydraulic pressure required to hold a stop. The hydraulic pressure must be at least be augmented by an electrically powered pump. In the remainder of the systems presented in this section, the hydraulic pump is powered by the electrical system.

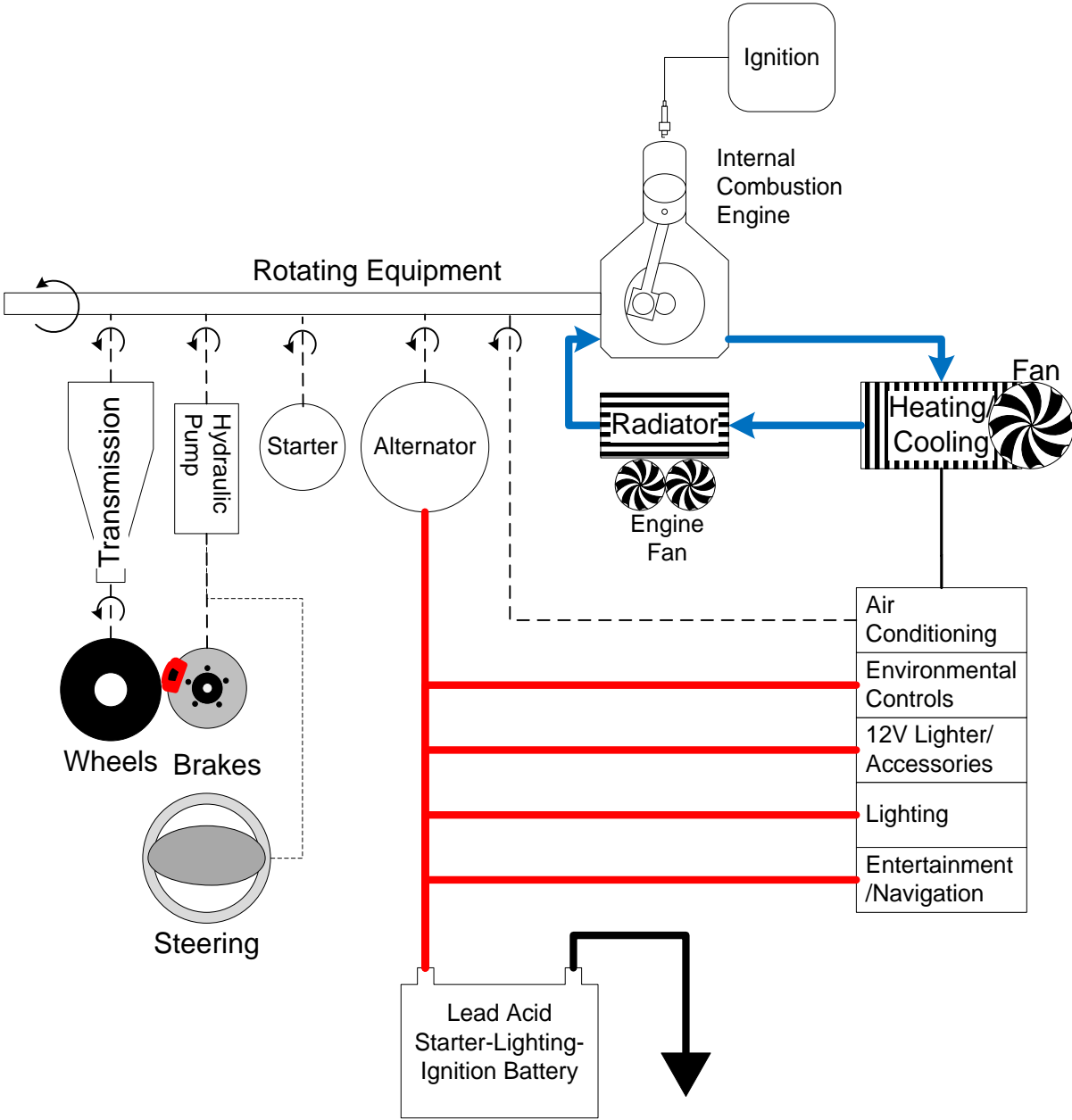


Figure 5-1. Traditional internal combustion engine system.

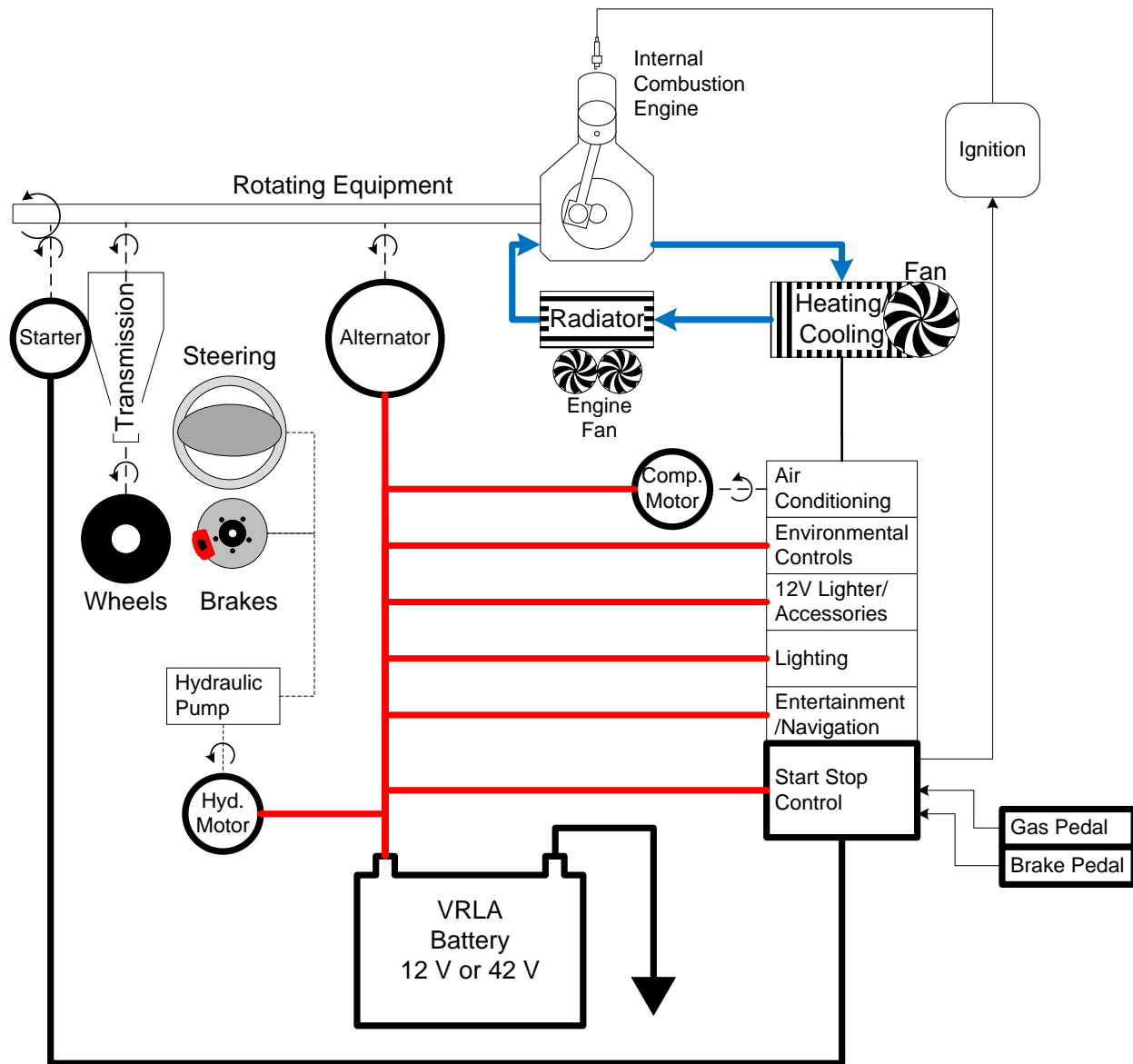


Figure 5-2. Micro hybrid electric vehicle system.

5.3 PHEVs

PHEVs differ from other HEVs in that the battery is recharged by a connection to the electric grid. Regenerative braking also recharges the battery. The electric drive train has the power needed to operate the vehicle through its full range of speeds over a nominal 40-mile operating range. The ICE may be used to increase performance. In normal operation the PHEV starts out operating solely off the battery. Once the battery charge has been depleted, the ICE engine drives a generator providing power to operate the vehicle and extending the operating range past the nominal 40-mile battery range. The battery is still used for regenerative braking to improve city driving gas mileage. The available energy in a PHEV battery must be much larger than in an HEV. The FreedomCAR energy requirement for a 3,300-pound passenger car with a 40-mile range is 3.4 kWhr to 11.6 kWhr, an order of magnitude greater than a strong HEV. A notional PHEV electrical system is shown in Figure 5-5.

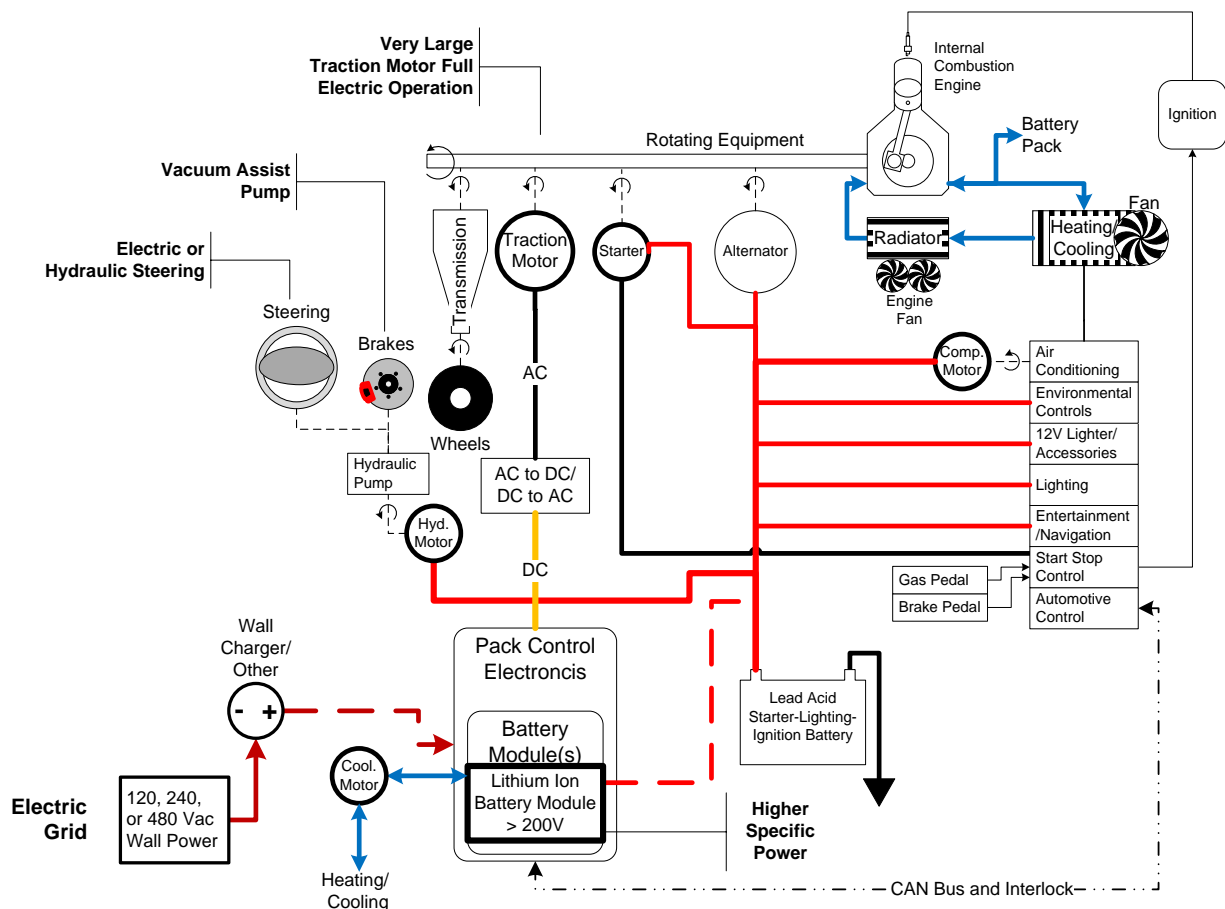


Figure 5-5. Plug-in hybrid electric vehicle system.

5.4 BEVs

In some respects, the PHEV and BEV are similar. They are similar in that they are both recharged from the electric grid and they are fully operational with battery power only. Both PHEVs and BEVs require high-energy batteries. Because the BEVs are lighter and have a lower power to weight ratio, the power requirements of a BEV are lower than those of a PHEV. Removing the ICE system components simplifies the BEV design as shown in Figure 5-6. The range of an HEV is about 100 to 200 miles, more than twice the PHEV range. Unlike the PHEV, once the battery has been depleted, the BEV must be recharged from the grid.

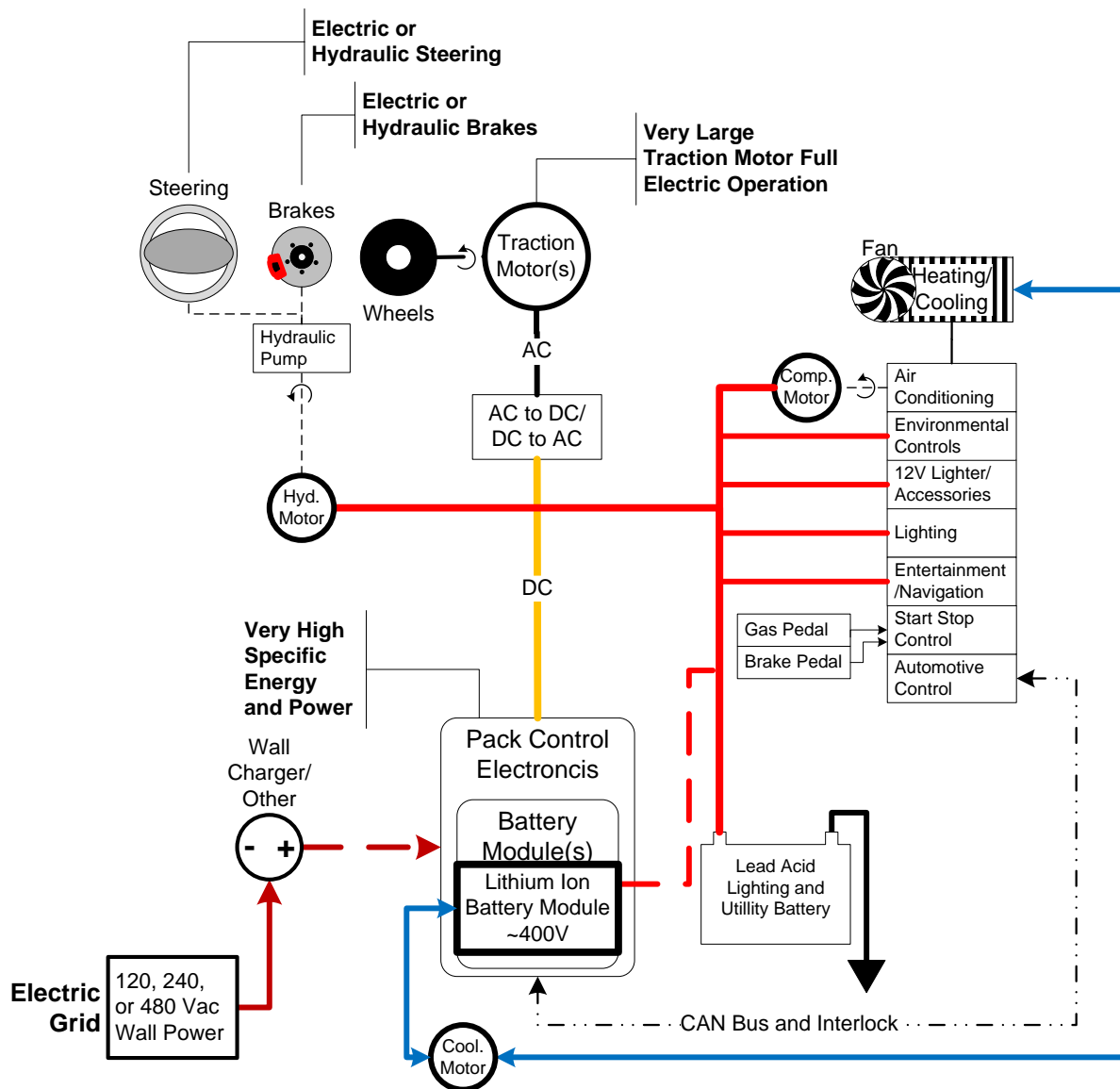


Figure 5-6. Battery electric vehicle system.

5.5 Summary

The difference between traditional ICE vehicle electrical systems and HEV and BEV increases from low to high in the following order.

- Micro HEV (Least different from ICE)
- Mild HEV
- Strong HEV
- PHEV
- BEV (Most different from ICE).

The Micro HEV primarily relieves the driver of tasks that could be accomplished manually. The Micro HEV, however, also increases the size of the traditional battery and available energy. The Micro HEV voltage is low, 12 V to 42V, and therefore below the nominal safety voltage threshold. This system does not benefit from energy recovering regenerative braking.

Mild HEVs add a larger battery operating at a nontraditional and higher voltage. This battery is primarily sized to capture regenerative braking energy. The battery must be able to absorb high-peak regenerative braking energy and provide high-peak discharge power to assist acceleration. The recovered braking energy is then used for ICE power assist on acceleration. Battery power is inverted into AC. Since the operating voltages are higher than 42 V, the electrical isolation requirements for DC and AC must be met. Operationally, a Mild HEV does not provide launch power.

A Strong HEV has a larger battery than a Mild HEV as well as larger electric motors. A Strong HEV provides enough power to launch the vehicle from a stop and can provide enough power to operate the vehicle at modest speeds without turning on the ICE. The operating voltage of the Strong HEV is higher than that of a Mild HEV, generally over 200 V. Higher voltages allow higher power distribution over smaller gauge wires. Electrical isolation is again a safety requirement for Strong HEV systems. The battery technologies may include nickel metal-hydride (NiMH) but are more likely to be composed of lithium battery chemistries. The control systems and safety requirements for lithium batteries are more complex than those of NiMH.

A PHEV is similar to a strong HEV in that they both provide enough power to launch and operate the vehicle at moderate speeds. Operating voltages are again high and direct current power from batteries is inverted to alternating current therefore isolation requirements also apply. Because PHEVs have much higher energy requirements, PHEV batteries are much more likely (or certain) to be lithium-based, and therefore carry the control and safety overhead not present with NiMH systems. Complex charging systems operating at high voltages unattended for overnight charging are required to recharge batteries. Recharging adds a new systems interface for the operator, home, and, if available, public recharge sites. These new recharging systems present a new area for system safety concerns.

BEVs are similar to PHEVs except that the batteries are larger, are most certainly based on lithium chemistries and may have even more aggressive recharging systems. A BEV does not necessarily present more safety hazards than a PHEV, but since the battery is larger, there is more available fuel if a fire were to start.

General characteristics across all battery vehicle types are compared in Table 5-1. A composite of HEV and BEV FreedomCAR performance targets is shown in Table 5-2. In the table there are entries for Mild HEV systems based on 42V electrical systems, low power assist (Mild HEV),

and High Power assist (Strong HEV), as well as high-energy and high-power PHEVs. The table shows that high power is more important for all of the HEV types except the high-energy PHEV as well as the BEV.

Table 5-1. Comparison of HEV, PHEV, and BEV characteristics.

Characteristic	Micro	Mild HEV	Strong HEV	PHEV	BEV
Target Weight (kg)	10	40	60	60 to 120	NA
Target Volume (l)	9	32	45	40 to 80	NA
Voltage (V)	42	42 to 200	> 200	> 300	> 300
Energy (kWh)	0.25	0.3	0.5	3.4 to 11.6	24
Regenerative pulse (kW)	NA	20	35	25	NA
Discharge pulse (kW)	6	25	40	38	NA
Plug-in recharge voltage (V)	NA	NA	NA	120 220	120 220 440

Table 5-2. Comparison of specific performance targets for HEVs and BEVs.

Vehicle Type	Specific Energy (Wh/kg)	Specific Power (W/kg)	P/E Ratio	Energy Cost (\$/kWh)	Power Cost (\$/kW)
Micro 42V	25	600	24	\$600	\$25
Mild 42V (low power)	12	520	43	\$867	\$20
Mild 42V (high power)	20	514	26	\$514	\$20
Power assist (low power)	8	625	83	\$1,667	\$20
Power assist (high power)	8	667	80	\$1,600	\$20
PHEV (high power)	57	750	13	\$500	\$38
PHEV (high energy)	97	317	3	\$293	\$89
BEV	200	400	2	\$100	\$50

6 Battery Management and Control Systems

Batteries for use in vehicles require management systems and control systems to ensure safe and efficient operation in highway service. This section presents the general approach to battery control, and the safety features required to limit the extent of any failures or anomalies. For example, a key challenge in battery control systems is the difficulty of measuring, estimating, or inferring variables given the changing conditions within the cell during operation and over its service life. The functions of battery management and control systems, including a series of subsystems or blocks, are presented, along with the inputs to those systems and their role in safe operation. The section also presents the prevailing methods and issues in control of battery charging and discharging, such as keeping the cell within the voltage operating range without excursions.

6.1 Control Approach

Earlier in the report, parameters were identified that define the safe operating conditions for the battery. For instance, it is common to limit the voltage, current and temperature to definite ranges that may be modified as a function of other parameters such as the SOC, temperature, battery age, or capacity. The safe operating region is discussed further in this chapter in a control context, including the ability of discrete measurements to safely summarize the state of the battery. For instance, to specify the state of a battery at any instant in time, quite a few variables are required. Some can be readily measured, such as voltage and current. Others can only be inferred with difficulty, such the chemical species and their concentrations as a function of position on the electrodes. These issues become especially important during highly transient operation, which is common in vehicle batteries. Essentially, this brings the operating history of the battery into consideration, since the species and concentrations evolve over time.

Although battery controllers estimate key variables such as the SOC and SOH, it is not clear that these variables plus the typically measured variables, i.e., voltage, current, pressure, and temperature, specify safe operating regions of the battery under all conditions. Consequently, additional safety features are generally required to limit the extent of a failure or anomaly, and provide protection for out of range parameters, such as current, cell voltage, pressure, and temperature. Some safety features are internal to the battery, such as current interrupts, shutdown separators and PTC materials. Others are external to the battery and are controlled by the battery control system. That control system is the topic of this chapter, but the discussion will draw heavily from the preceding chapters, repeating information where appropriate. In Chapter 4 a conceptual design for a battery system was presented, including the layout for the control system. Here we discuss those control issues in more detail and present a summary of another BMS from the literature.

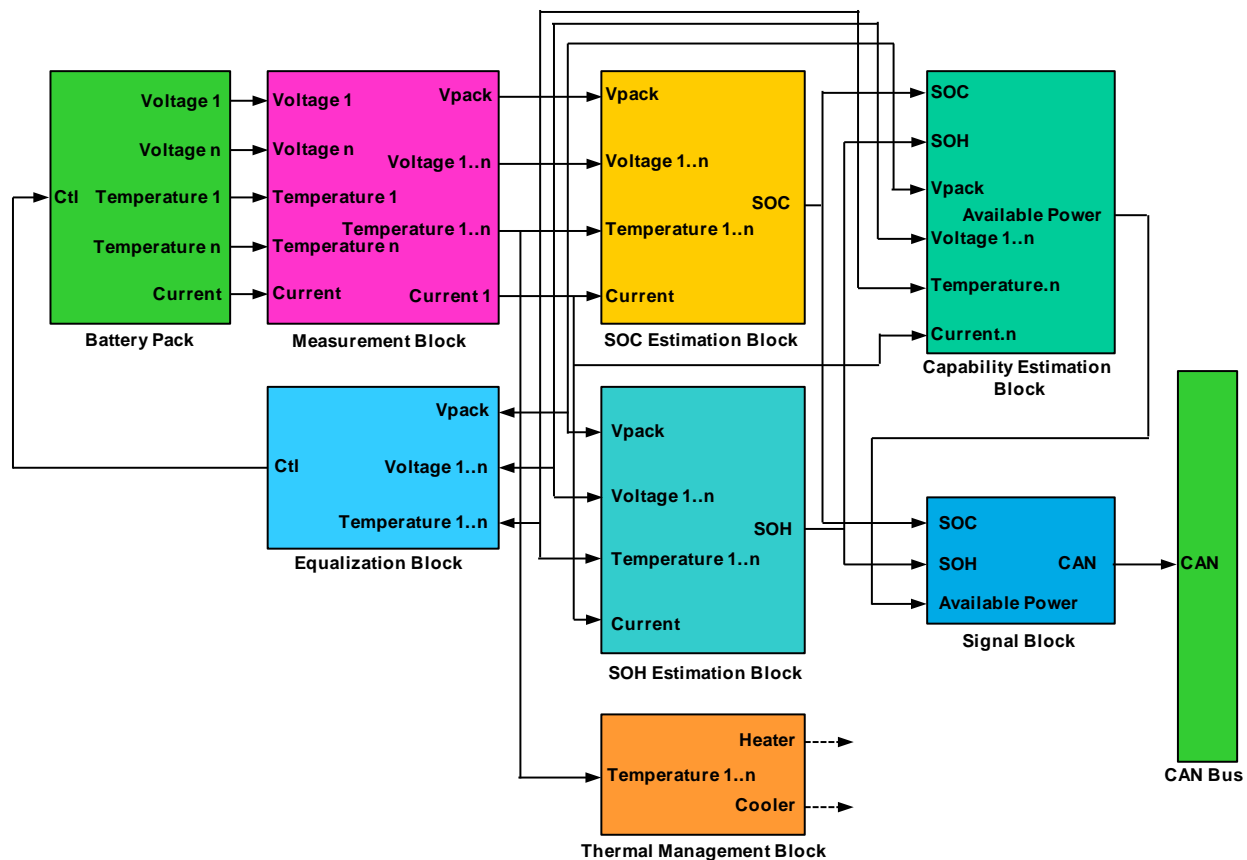
A common theme in the chapter is the challenge in measuring, estimating, and inferring variables that are needed for control. This challenge arises because of several topics that were previously discussed, such as the cell-to-cell variations in voltage and capacity, which are inevitable due to manufacturing tolerances, both in geometry and materials; stress and aging of the battery components; thermal gradients within the pack; and the presence of impurities and local side reactions. Another challenge comes from using overall cell measurements of voltage and current to predict safety and performance phenomena, such as side reactions, that involve more fundamental variables: the voltage and species composition on a specific electrode.

6.2 Battery Management and Control System Functions

In Chapter 4, a preliminary concept design for a battery system was presented as a starting point. In the next section, charging and discharging controller background are presented. Here we discuss a recent paper on BMSs and the control functions they present. This overall controller design is similar to that in Chapter 4 at a high level, and provides another example of a BMS. In this paper by Cheng, Divakar, Wu, Ding, and Ho (2011), the BMS consists of the following subsystems, described in Table 6-1 and illustrated in Figure 6-1. The input/output function and required measurements of each of the supervisory controller subsystems are shown.

Table 6-1. Supervisory controller functions.

Supervisory Control	Input	Control Function	Safety Role
Measurement	Measures cell voltage, current, temperature on case locations and ambient	Sample data. Cell voltage indexes from cell to cell at each sample time	Provides input for algorithms and checking of safe range
Battery Algorithm Capacity SOC/SOH	From Measurement Block	Determines SOC, SOH,	Often used in capacity estimation to reduce risk of overcharge and over discharge
Cell Equalization	Voltage from Measurement Block, SOC from Algorithm	Either dissipative or active cell balancing enforcing $V_{min} < V_{cell} < V_{max}$ or methods are used to tolerate imbalance	Overcharge/discharge thermal runaway, temperature rise, specified voltage range, gas generation, etc.
Thermal Management	Temperatures from Measurement Block, cooling flow rates or power, heater power	Cooling and heating activation, to maintain specified temperature range.	Temperature rise, thermal runaway, capacity fade, self-discharge, low temperature performance.
Capability Estimation	SOC, SOH from Algorithm Block Temp, Current, Voltage from Measurement Block	Determine maximum charge/discharge current at any instant in time and send to vehicle ECU	Sets overcharge/overdischarge limits



Source: Cheng, Divakar, Wu, Ding, and Ho (2011).

Figure 6-1. Subsystems in a representative battery management system.

The BMS in Cheng, Divakar, Wu, Ding, and Ho (2011) consists of the following blocks.

6.2.1 Measurement Block

The measurement block measures and digitizes individual cell voltages, current, ambient temperature, and surface temperatures at various locations on the battery case. Measuring individual cell voltages is crucial, as previously discussed. The measurements are made by sampling one of the cell voltages at each sampling time and indexing to the next cell at the next sampling time.

6.2.2 Battery Algorithm Block (State of Charge and State of Health)

The battery algorithm block estimates SOC and SOH, which can be critical parameters for safety and performance in many designs (Cheng, Divakar, Wu, Ding, & Ho, 2011), using measurements at regular intervals of cell voltage, current, operating cycles, age, and temperature. The measurements are input into a battery model for the estimation. Cheng, Divakar, Wu, Ding, and Ho use a lumped parameter battery model with a polynomial fit between the open circuit voltage and the SOC to derive a state space representation of the system. Errors between predicted and measured battery voltage are used to correct the SOC with a Kalman filter.

6.2.3 Capability Estimation Block

The SOC and SOH are used in the capability estimation block to find maximum charge and discharge currents, predict available power, and, presumably, to set limits on other operating parameters, such as cell voltage, although that is not stated.

6.2.4 Cell Equalization Block

As discussed previously, all cells do not perform identically, and active cell voltage balancing is often used prevent unsafe operation, performance loss, and capacity degradation. In the approach of Cheng, Divakar, Wu, Ding, and Ho, the maximum voltage difference between cells is found, and if the difference exceeds a set limit, charging stops and the highest voltage cell is partially discharged through a resistor. Although, this is a dissipative approach, active cell balancing is also discussed. This approach, which is more efficient but more expensive, can charge cells individually or transfer charge among cells. Other approaches are discussed in Moore and Schneider (2001) and Cao, Schofield, and Emadi (2008).

6.2.5 Thermal Management Block

Controller decisions are often based on temperature estimation given a limited number of measurements within each battery pack, with extrapolation based on a simple 1D temperature-estimation method. For ordinary operation, this is straightforward despite a large variation in current and voltage. However, for unusual loads or thermal events, incomplete temperature data is a concern. Because of strong local heating during a thermal event, the measured temperature may differ substantially from the local temperature. For instance, experiments by Leising, Palazzo, Takeuchi, and Takeuchi (2001) showed that temperatures on the exterior of the case during overcharging were up to 40°C lower than the internal temperatures. In a more extreme example, Dahn (2001) found that a nail instrumented with a thermocouple showed $T > 600^{\circ}\text{C}$ when used for short circuit testing (slow penetration). Spotnitz and Franklin (2003) reported on a test by Kitoh and Nemoto (1999), who found that a nail penetration test at 1 mm/s yielded a maximum temperature of 380°C. With such high local heating, the temperature at the measurement location may lag behind the local temperature. Consequently, temperature measurement locations and estimation methods can be critical during thermal events to enable time for mitigation equipment to respond.

Overall, the thermal management block keeps the battery within the safe and effective operating range. Generally it uses battery and ambient temperatures to control heating and cooling, along with monitoring for excessive temperatures, and initiating of safety steps during a thermal event.

6.3 Charging and Discharging Control

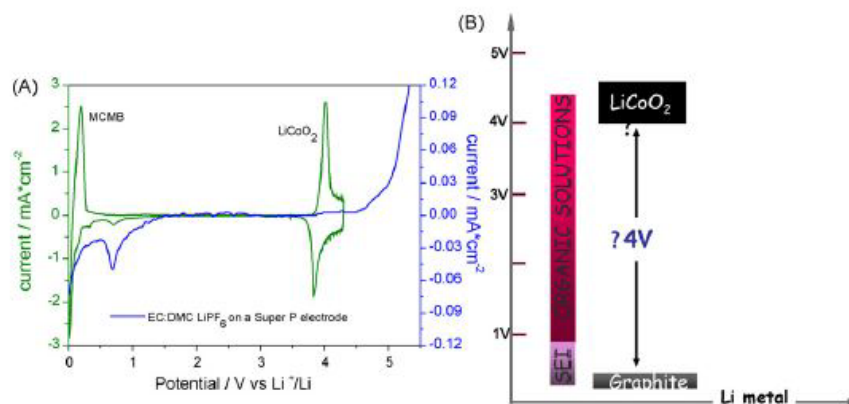
The battery controller orchestrates the charging and discharging process, managing time-varying loads and battery conditions with high energy efficiency. It maintains the battery operating variables within the safe range, while monitoring and controlling individual cell voltages and equalizing voltage between the cells, which may help to minimize the possibility of overcharging or over discharging an individual cell. Other possibilities include control limits on each individual cell. Battery control in vehicles is a challenging process: the loads can be highly transient and the battery may rapidly switch from charging to discharging using multiple charging and discharging rates (Bitsche and Gutmann, 2004). The rates can be high: in HEVs they can reach 20C. (C is a common unit for charging and discharging rates of batteries: 1C

discharge means that the capacity will be discharged in 1 hour.)

In the event of an unexpected occurrence, either the battery must passively manage it or the controller must diagnose it and control it safely. For instance, in a crash, the battery must be isolated to prevent hazards to passengers and first responders. In the event of a short circuit or other local event, the battery or the controller must limit the current, vent gases in case of overpressure, and isolate the battery if necessary.

6.3.1 Phenomena

While the failure phenomena have been discussed extensively in previous chapters, here we summarize these phenomena in terms related to the control systems and their actions. The cyclic voltammagram (CV) in Figure 6-2, reproduced from Scrosati and Garche (2010, Figure 4), shows many of the issues that the controller must address. In a CV, which is a common characterization measurement for electrochemical systems, the cell voltage is swept in a triangular waveform, and the current from the cell is measured to understand the response at different voltages and sweep rates. In Figure 6-2, the applied potential is relative to Li metal as a reference, and we see two large peaks in current: one at 0.15 V and one at 4 V. Thus the cell is designed to operate where it is most responsive, giving a cell voltage of about 3.85 V (in this example). The peak at 0.15 V corresponds to intercalation of Li-ions on the graphite anode, which is close to that of Li formation at 0 V, so Li metal can be easily formed. This proves to be a particular concern during charging at high states of charge where the anodic voltage can drop close to 0, due to increased voltage losses as charging forces ions onto the remaining electrode sites. The electrolyte (blue curve) should be flat if no reaction is occurring over the operating voltage range, but instead it reacts within the operating range of the battery, suggesting that electrolyte reactions and stability may be a problem. Indeed, it is well known that the graphite electrode and electrolyte react. However, by design, a passive layer is formed on the first discharge that shuts down the graphite-electrolyte reaction, but allows Li-ions to pass through. If this layer degrades over time, for instance because of volumetric changes in the electrode during intercalation, then the electrode and electrolyte react. At the cathode, we note that the cathodic potential is close to the electrolyte upper reaction boundary of about 4.6 V. So charging to a voltage near 4.6 V could lead to decomposition. Consequently, we can see the main controller issue: keep the cell within the operating range defined by the major peaks, without excursions to the undesirable side reactions just outside this range. In an operating battery there may not be a reference electrode, so only the voltage difference is measured between the anode and cathode. Unfortunately, this does not allow one to know the individual anodic or cathodic voltages, so it is only by inference that one is able to estimate the proximity to initiating the side reactions.



Source: Scrosati & Garche (2010).

Figure 6-2. Cyclic voltammogram.

Several approaches are used to overcome this problem. The first is empirically setting the allowable voltage, current, and temperature ranges to maintain a sufficient margin with respect to undesired behavior. The second is to use a model, combined with data, to infer the operating margin more carefully. Models may be simple or complex; the various types are discussed briefly in this chapter.

6.3.2 Charging

To avoid the electrode and electrolyte problems that occur during charging at high SOC, a common charging method has been developed. Li-ion batteries are usually charged at constant current to a voltage near the maximum, then held at constant voltage until the current declines to a preset value (about 3% of rated current) (Buchmann, 2011). The demands are high on the charger: charging outside the voltage range at high SOC can result in the plating of Li metal (which can lead to internal shorts), electrolyte breakdown, and oxidation of the cathode, releasing gas, particularly oxygen. Since cell-to-cell variations are common, equalization circuits or other means of dealing with the variability are required. Cells may be charged on an individual basis, and not as a pack. The charging tolerance is tight: ± 0.05 V/cell (Reddy & Linden, 2011). Since the cell cannot take an overcharge, trickle charging is not used, although a topping charge may be periodically applied when the voltage drops below a preset value.

Because of the varying conditions such as ambient temperature, thermal loads, age, and transient operation, the charging current is often specified as a function of key variables, especially SOC, temperature, and voltage. A microprocessor is used to compute these and other battery parameters (Doerffel & Sharkh, 2006).

At low SOC, higher charging currents (up to the maximum allowed) can be used (Moore and MacLean), and this is often done. However, this approach requires a reasonable estimate of SOC for safe charging. Since SOC alone does not fully describe the fundamental issue of keeping the electrode voltage away from the region where undesired side reactions can be excited, the charging currents, voltage limits, and temperature limits are set conservatively. Adding to this is the need to efficiently incorporate sudden inrushes of charge, such as from regenerative braking in HEVs. Consequently, the SOC may be held at lower than 100% during normal operation (Karden et al., 2007; Moore & MacLean).

Model-based Controllers

Model-based control of charging is a more advanced method. Different modeling approaches are being aggressively investigated, including equivalent circuit models, which are more commonly used, and electrochemical models, which are in the research stage (Chaturvedi, Klein, Christensen, Ahmed, & Kojic, 2010; Smith, 2010; Plett, 2004a, 2004b, 2004c).

Equivalent circuit modeling fits experimental data to a lumped parameter model of the battery that contains discrete components, such as resistors and capacitors (Chaturvedi, Klein, Christensen, Ahmed, & Kojic, 2010). Different battery response tests are used to ensure a reasonable fit, but unless the state space that the battery response encompasses is fully exercised in testing, the model may not cover all situations. This is particularly true when small AC signal perturbations about steady-state operating points are used, which is commonly done in impedance spectroscopy approaches.

Electrochemical models seek to describe the electrochemical processes in the battery with sufficient accuracy for charging and discharging control under a wide variety of circumstances (Chaturvedi, Klein, Christensen, Ahmed, & Kojic, 2010; Smith, 2010; Plett, 2004a, 2004b, 2004c). Since detailed models are too computationally intensive for use in vehicles, the models are simplified using a variety of techniques, including spatial averaging, frequency domain methods, partial analytical solutions, and series or function expansions. Proponents claim that model-based charging can be done aggressively, since side reactions are monitored by the model (Smith, 2010; Plett, 2004a, 2004b, 2004c). However, electrochemical models are at an early stage of development, and the appropriate approximations and control strategies are still under development.

State Estimators

Since the effect of charging current on voltage is explicitly tied to state of charge, and because other parameters are needed, such as SOH, battery controllers approximate these states and others using a combination of measurement and estimation. The simplest method to determine the SOC is coulomb counting, which simply integrates the current over time to get the net charge stored in the battery. However, this method is prone to error accumulation, and more refined methods are under intense development. With some modification, the same modeling types discussed earlier can be used for state estimation. Generally these include parametric models or expressions (Saha et al., 2007), equivalent circuit models, neural network and fuzzy logic models (Lee et al., 2008), as well as hybrid approaches (Coleman, Lee, Zhu, & Hurley, 2007; Codeca, Savaresi, & Rizzoni, 2008). At the advanced stage are model-based state estimation methods, such as ensemble Kalman filtering (Plett, 2004a, 2004b, 2004c; Santhanagopalan & White, 2008), which combine measurement and modeling to arrive at the SOC, SOH, and other parameters (Pop, Bergveld, Notten, & Regtien, 2005). These intelligent estimators offer a way of including battery aging and capacity fade, along with other changes, in the predictions.

HEVs require precise estimates of SOC, along with predictions of available power and SOH. Such vehicles use continuous cell balancing. BEVs have somewhat less stringent requirements, especially on SOC, since battery operation is less transient than that of the HEV. HEVs can require current rates of $\pm 20C$ compared to $\pm 5C$ for BEVs. HEVs are rarely in an equilibrium state, so measuring cell voltage alone is not sufficient to reliably determine SOC (Plett, 2004a).

Recent work on advanced charging and discharging techniques has clarified some of the side reaction phenomena, particularly Li plating on the anode. Smith (2010) used a fast executing,

reduced-order model to predict the voltage margin against Li plating and showed that controlling to a specified margin offered a less conservative strategy than setting cell voltage limits. Furthermore, as the battery ages, simply setting voltage limits may not be conservative against side reactions (Chaturvedi, Klein, Christensen, Ahmed, & Kojic, 2010), potentially leading to unsafe operation.

6.3.3 Discharging

Steady discharge at a high rate can lead to nonuniform concentration of active species, causing the cell voltage to drop below the cutoff voltage, usually about 2.7 V, and the cell to shut down. Pulsed discharge (down to the cutoff voltage) gives the ingredients time to diffuse and reduce the nonuniformities. Consequently, the dynamics of the discharge current influence the cell potential and the performance (and hence safety) (Chiasserimi, 2001). Because these phenomena are fundamentally different than high-current charging, the maximum allowed current is usually different in charging and discharging, with the maximum discharging current being larger.

The lower cutoff voltage is set because of copper dissolution from the current collector and redeposition on the anode, reducing life, reducing performance, and potentially causing dendrites to form, which could lead to internal shorting.

Similar to charging, advanced controllers at the research stage seek to replace the lower voltage discharge limit with a more fundamental estimate. For instance, Smith (2010) suggests a lithium concentration limit at the reaction interface, which must be obtained by a reduced-order electrochemical model. Smith, Rahn, and Wang (2010) calculated that the surface concentrations governed the interfacial potential and discharge current, not the bulk SOC, which is commonly estimated. These effects are expected to be more important during times of rapid depletion of Li-ions on the surface, such as high discharge currents, when diffusion limits the transport from the bulk to the surface.

6.3.4 Cell Balancing

As previously discussed, without cell equalization controls and individual cell voltage monitoring, cell-to-cell variations could lead to out of range parameters in one or more cells. Since Li-ion batteries cannot tolerate overcharging without risk of electrolyte breakdown or damaging side reactions, designers cannot rely on average behavior of the pack, nor can they use the simple balancing methods that lead-acid and nickel batteries use. A variety of techniques for balancing cells have been proposed and used (Moore & Schneider, 2001; Cao, Schofield, & Emadi, 2008), including dissipative and non-dissipative shunting methods, switched capacitive shuttling methods, and converter methods. Even with these approaches, individual cell voltages are carefully monitored, and charging and discharging controls are focused on the individual cells and not the pack.

HEVs and BEVs may use different cell balancing approaches. BEVs are generally fully charged after each use cycle, but HEVs may partially charge the batteries to allow extra capacity to accommodate sudden regenerative braking currents. Thus, methods that move charge at high SOC are not generally appropriate for HEVs. Moore and Schneider (2001) identified dissipative and shuttling methods as most appropriate, although the extra cost and complexity for shuttling was a concern. Cao, Schofield, and Emadi (2008) recommended switched capacitor methods for HEVs and boost shunting for high-power applications. Boost shunting uses an equivalent buck-boost converter to move energy from the high-voltage cell to other cells in the series.

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7 Battery Conditions That Enhance the Initiation and Growth of Internal Shorts

7.1 Background on Internal Shorting

Thermal runaway and thermal stability of batteries has been covered in earlier chapters of this report, as well as in the technical literature. Here we focus on a topic that is less well known: the role of side reactions that can lead to internal short circuits (shorts) and the influence of the operating conditions on the initiation and growth of these events. The initiation of these shorts can be the first step in a cascade that leads to thermal runaway and other safety and performance events (Mikolajczak, Kahn, White, & Long, 2011). Ultimately, the goal is to provide information that can be useful in defining a simulated driving cycle suitable for safety testing of Li-ion batteries.

The problem is complicated by both the complexity of the science behind Li-ion batteries and the diversity of battery chemistries and designs. The field is quite active with many new chemistries being explored to solve the challenges for electric vehicles, and so safety related observations have to be generic enough to encompass the diversity of batteries and specific enough to evaluate problems with specific chemistries and designs. Here we focus on the formation of internal shorts, primarily due to metal plating, and recognize the different, specific reactions that occur.

Internal shorts are a major mode of Li-ion battery failure, and in at least one study, the most common mode (Ofer, McCoy, Barnett, & Sriramulu, 2011), although the incidence of occurrence is small—1 internal short in 10 million cells according to Ofer, making detection extremely challenging. However, with battery packs that contain 1,000 cells per vehicle, the vehicle failure rate could approach 1 in 1000. Consequently, shorts are hard to find, but significant to safety. Fortunately, most internal shorts only cause the cell to fail, without leading to thermal runaway or other incidents.

When shorts do lead to thermal runaway, they create a conductive path between positive and negative cells, growing a conductor from one electrode to the other by puncturing the separator. The conductive path is usually caused by metallic bridging or dendritic growth of a metal on one of the electrodes.

Because shorts grow subtly and the occurrence is low, the precursors are hard to detect by the manufacturers when the battery is new, although manufacturers often use advanced diagnostics to search for metallic particles and other out of specification conditions. Methods are just now being developed to investigate incipient shorting behavior (Ofer, McCoy, Barnett, & Sriramulu, 2011; Keyser et al., 2011, Mikolajczak, 2011). Standard nail penetration tests, where a nail is driven into the cell at a prescribed location and rate, do not seem to capture the phenomenon involved in internal shorts that grow slowly due to dendritic formation by electrochemical phenomena (Ofer, McCoy, Barnett, & Sriramulu, 2011). However, it is interesting that the nail penetration tests can result in temperatures over 600 C along the path of the nail, and that is strongly a function of the penetration rate.

Conventional methods of shutting down the cell, such as shutdown separators and PTC devices, may not work in cells, especially large format cells, with an internal short. This is because the

short is a local event, with a locally high temperature, but the remainder of the separator and cell may be at an acceptable temperature for some time after the short (Kim, Smith, & Pesaran, 2011a).

Shorts have been hypothesized to be initiated by several mechanisms:

- Metal can be formed by electrode or contact dissolution and subsequent plating or by lithium metal plating on the anode or some combination.
- Unintended metallic particles may be present in the cell. However, in this chapter we will focus on the metallic deposition.
- Non-metallic conductive debris, such as carbons and electrode fragments from handling.

Recent work by Ofer, McCoy, Barnett, and Sriramulu (2011). concluded that cathode metal dissolution with anodic plating was the most common short initiation mechanism.

Here we will primarily focus on shorting that is causing by metal plating on at least one electrode, but other shorting types are also possible. Keyser et al. (2011). considered shorts that originate between the current collectors, between the electrodes, and between a collector and an electrode. They show clearly that the thermal response and tendency to achieve thermal runaway are different with small cells than with large cells.

To protect against safety issues, capacity and durability loss, as well as performance loss, measurements are made of the voltage of each series element within an operating vehicle, along with current at appropriate stages in the system and temperature at selected, discrete locations. These measurements are then used in an algorithm that essentially predicts an allowable operating window. However, the side reactions that occur are determined by the local interface potential within an electrode-electrolyte pair and not by the cell difference. Since individual electrode voltages cannot be directly measured, electrochemical reactions are described by relating the voltage to a reference voltage. This is in contrast to the practical measurement of cell voltage, which measures the voltage of one electrode relative to the other, not to a standard reference. Since both electrode voltages change as a function of the current through the cell and other operating conditions, the voltage on each electrode can only be approximated. So a central problem in protecting against the initiation of dissolution and metal plating is the relating the variables that can be measured in a battery under actual operating conditions to the interfacial voltages, currents, and temperatures that govern the dissolution and plating phenomena.

In this chapter we first discuss recent examples of the technical literature on each of the major side reaction mechanisms that can lead to internal shorts. We focus on lithium plating, internal resistance growth, copper dissolution, and cathode material dissolution, with some discussion of general capacity fade and self-discharge over time. Next we use a mathematical model of the Li-ion battery to illustrate the phenomena that can lead to potentially damaging side reactions, and ultimately relate that to operating conditions that can accelerate these reactions. Because there are multiple battery chemistries and designs, we illustrate the performance for a relatively common cell, the lithium manganese oxide (LiMn_2O_4) cathode with a graphite anode electrolyte. The model is a standard model in Comsol 3.5a and is based on the Newman model (Fuller 1994), which has been validated and is widely used.

For this model, we do not seek to compute the amount of deposits that may form on an electrode, but simply illustrate the electrode voltages that can drive the side reaction for a given set of operating conditions. This is not meant to be an exhaustive study of side reactions and loss

mechanisms, but rather an illustration of the effect of the operating conditions on the possibility for some of these reactions to occur.

7.2 Operating Window for Li-ion Batteries

As we have discussed earlier, numerous approaches are being used and explored for defining a safe and durable operating window for Li-ion batteries. Generally, these are related to parameters that can be economically measured: the cell voltage, current, and temperature at discrete locations. The lower voltage limit is usually about 2.7 to 3 V with an upper limit of about 4.2 V. The specific values depend upon the battery chemistry, design, and expected operating cycles.

The side reactions that lead to metal plating—as well as reductions in capacity, life, and performance—depend upon the voltage on an electrode, which is different from the cell voltage, and upon the local temperature in the battery, which can be different from the temperature at the measurement locations.

The cell voltage is related to the voltage at each electrode through electrochemical principles. First, the voltages of the negative and positive electrodes are defined as E_n and E_p , respectively. The cell voltage is then $E_p - E_n$. When no current is flowing in the battery, the battery achieves an open circuit voltage, and the voltage on each electrode becomes E_{n0} and E_{p0} . This open circuit or equilibrium voltage is related to the free energy of the electrochemical reaction, which is a function of the concentration of reactant and product species and the temperature. So as the battery charges and discharges, these concentrations change and the open circuit voltage changes.

In the simplest form, a prototype reaction of interest is $M = M^+ + e^-$ at a certain voltage E_0 . If the electrode potential is positive with respect to E_0 , the reaction shifts to the right; if the potential is negative with respect to E_0 , the reaction shifts to the left. Multiple reactions of this type are possible in batteries. For example, the intercalation of lithium on graphite occurs at about 50 mV compared to a Li/Li⁺ reference electrode, the lithium plating reaction occurs at 0 V, and the copper dissolution reaction occurs at about 3.4 V.

Although the equilibrium current is zero for the open circuit voltage, it can be represented as the sum of a cathodic and anodic current, each equal and occurring in opposite directions. To produce a net current in one direction, the voltage must be changed from the equilibrium voltage, and this deviation is defined as the overvoltage of a specific reaction on a specific electrode: $\eta_n = E_n - E_{n0}$ and $\eta_p = E_p - E_{p0}$. The current produced by the overvoltage is defined by the Butler-Volmer equation and is a strong function of the overvoltage.

$$j_i = i_0 [e^{\alpha \eta_i F / RT} - e^{-\alpha \eta_i F / RT}] \quad (7-1)$$

where the subscript i refers to either the positive or negative electrode.

Both the η and j vary as a function of position within the electrode and with time. Using the definition of η , the equation can be rewritten as:

$$j_i = i_0 [e^{\alpha (E_i - E_{i0}) F / RT} - e^{-\alpha (E_i - E_{i0}) F / RT}] \quad (7-2)$$

where

j is the current per square area, usually called the current density
 i_0 is the exchange current density, which is also a function of the reaction rate constant, the species concentrations, and the temperature, and is defined for a specific reaction on a specific electrode
 α is the transfer coefficient, which is defined for specific reactions
 F is the Faraday constant
 R is the gas constant
 T is the temperature.

So for a given current density profile in an electrode, we can determine the overvoltage η and then the voltage profile in the electrode from the relation $E_i = \eta_i + E_{i0}$. So for a cell that is designed to operate within a particular window of cell voltage, with that window designed to keep the individual electrode voltages within a safe range, we can develop out of range voltages if the coefficients in Equation 2 change significantly beyond the design values. These coefficients primarily include i_0 and E_0 , which are at least functions of concentration and temperature, and may also change with local geometry and contaminants on the surface.

To compute these quantities with reasonable accuracy requires additional equations, including transport equations for charge and species. This has been worked out by many authors and is discussed in more detail in Section 7.4.

In addition, the overvoltage changes due to the operating conditions. For instance, in charging the negative electrode, more potential drop is required to push electrons across the interface as the sites fill and the state of charge increases.

Also, not only the distribution of species within the cell, but also the amount of cyclable lithium, can change over time. Christensen and Newman (2005) pointed out that cyclable lithium can be added or removed by side reactions at either electrode, and that the amount of active lithium also depends upon the capacity of each electrode and how well the electrodes are balanced. In addition, as the cell ages and capacity is lost, with changes in electrode structure and composition, electrolyte chemistry, thermal phenomena, and even supporting material structure and composition, the coefficients may change further.

The design of the cell is also critical. The capacity of the anode and cathode must be balanced to avoid high polarization in the lower capacity electrode that can push the voltage into the side reaction range.

Each reaction, both desired and undesired, is generally represented by an approach similar to the discussion above. The main reaction is the lithium intercalation within both electrodes. However, if the overvoltage for the reaction becomes sufficiently high, the side reaction rates could increase and initiate undesired effects such as metal plating. The next section describes side reactions, their effects, and the conditions upon which they occur.

The understanding of safety mechanisms in Li-ion batteries is not fully developed. For instance, in a recent talk, Orendorff (2011) noted that the effects of cell aging (capacity loss, metal deposition, etc.) are not well known in their effects on safety and abuse tolerance.

Operation within the allowable window is maintained by the battery management system, which considers cell-to-cell variations and cell balancing, and enforces the window parameter limits. Failure of critical functions of the BMS can lead to operation outside the allowable window, so that needs to be considered as well.

7.3 *Undesired Side Reactions and Loss Mechanisms*

7.3.1 Lithium Plating

During charging, the sites of lithium intercalation in the graphite electrode progressively fill, which increases the resistance across the interface and forces the electrode voltage to be more negative with respect to equilibrium. If the voltage becomes low enough, the lithium plating potential is reached and lithium forms on the electrode. Lithium will plate when $E_n < 0$. This is more likely to occur with conditions that increase the intercalation overvoltage during charging: high charging rates, low temperature, and reduced negative electrode capacity compared to the positive electrode. Overcharging can also force lithium plating by filling the available intercalation sites, and the excess current can go into depositing lithium.

Lithium dendrite formation has a long history—in fact lithium metal batteries of the 1970s were limited by dendrite formation from the lithium metal negative electrode that led to shorting and safety problems (Tarascon & Armand, 2001).

Monroe and Newman (2003) modeled dendritic growth in lithium-polymer cells. Liu, Kunz, Chen, Tamura, and Richardson (2010) examined LFP cells under cycling and used a small reference electrode. They showed the negative electrode potential going over 1 V at zero state of charge and reaching 0 V at 100% SOC, where lithium plating could occur.

Tang, Albertus, and Newman (2009) modeled lithium deposition, showing that geometrical effects on the electrode are important for plating and that one-dimensional models cannot capture them. Edge to center potential differences have been measured at up to 1 V, and local voltages reached 4.6 V, which is high enough to oxidize solvents at the positive electrode. Tang, Albertus, and Newman used a two-dimensional model to determine the conditions that created favorable voltages for lithium deposition—that is local voltages < 0 V. They showed that voltages < 0 were reached even though the cell V was less than the cutoff voltage of 4.2 V. They also showed that geometry modifications could mitigate this effect. The solution was sensitive to the kinetic constants: with a reaction rate constant cut in half, lithium deposition occurred before the cell voltage limit was reached and geometry modification did not help; with twice the constant, the cell voltage limit was reached first. By investigating the influence of charging rate, they found that charging at C/2 reduced the overvoltage sufficiently so that the cell voltage cutoff was reached before lithium deposition occurred. In contrast, charging at 2C increased the overvoltage sufficiently so that deposition occurred before the cutoff, and geometrical modifications could not mitigate this. They also showed that increasing the electrolyte conductivity allowed the cutoff voltage to be reached before the lithium deposition began, but this was also a function of capacity ratio between positive and negative electrodes. Separator thickness and electrode gap also influenced lithium plating.

Arora, Doyle, and White (1999) modeled lithium deposition on the negative electrode during overcharging of Li-ion batteries. They noted that the exchange current density for lithium plating is high: 2 to 36 mA/cm², indicating that lithium readily plates. Like Tang, they considered the balance between anode and cathode capacity. A cell with excess negative electrode capacity did

not reach lithium plating potentials even when the cell was overcharged to 4.45 V. However, the excess capacity may cause a loss of performance.

Smart, Whitcanack, and Ratnakumar (2007) showed that charging at low temperatures (-40°C at C/20 rate) resulted in lithium plating in a prototype cell. Charging at room temperature did not result in measureable lithium plating on a discharge curve. In one example, charging at -20°C with a cell cutoff voltage of 4.1 V resulted in negative anode voltages throughout the entire charge cycle. However, this paper concerned a space application, and motor vehicle manufacturers generally do not charge batteries at -20°C . In other cases, negative electrode voltages below zero during charging did not result in measureable lithium plating during discharge, at least by observing the discharge curve.

Mikolajczak, Kahn, White, and Long (2011) discussed findings on lithium dendrite formation, noting that it occurs during charging and that many failures that they studied initiated after or during charging, even if the batteries had long periods of normal use. They point out that small, isolated dendrites may not be a problem because the subsequent shorting current may rupture the dendrite due to resistive heating. However, this can lead to a layer of disconnected lithium dendrites that assist local currents in future shorts or participate electrochemically in other reactions. Dendrites large enough not to rupture during joule heating appear to be a viable path to thermal runaway.

7.3.2 Electrolyte Breakdown and Resistive Film Formation

The electrochemical stability of the electrolyte is typically exceeded by the operating voltage range of Li-ion batteries, resulting in the formation of the SEI layer during the first discharge on the negative electrode surface (occurring during the first cell charge). The layer formation consumes active lithium and limits capacity as the layer grows. The layer can grow during storage, and can grow or be suppressed by cycling. However, other solid surface films that are resistive can also grow with cycling (Smith, Kim, & Pesaran, 2009).

Studies that were reviewed on electrolyte breakdown and resistive film formation focused primarily on performance fading issues. However, since these can result in overvoltage changes, they are considered are possible precursor events for incipient shorting. This topic remains to be explored further.

Ning, White, & Popov (2006) modeled the cycling behavior of Li-ion batteries during resistive film formation due to electrolyte reduction that irreversibly consumed active Li-ions and formed a resistive film at the anode-electrolyte interface. Similarly, self-discharge has been modeled due to a solvent reduction reaction, estimating the growth in the resistive layer on the carbon electrode and the change in open circuit voltage, capacity, and state of charge with time (Ramasamy, Lee, & Popov, 2007).

Ramadass, Haran, Gomadam, White, and Popov (2004) gave a capacity fade model that can be used to predict the voltage on the negative electrode when a resistance layer has formed due to solvent reduction. The dissolution reactions are large in number and more difficult to quantify. The SEI is known to be stressed due to volumetric changes as lithium is inserted into the graphite electrode, causing the layer to be broken, formed, and reformed throughout the cycle. The growth in the layer can result in higher overvoltages because of the increased resistance. In addition, active material is lost through reaction with the SEI layer. The simplest reaction is the reduction of EC electrolyte, which is commonly used and is assumed to occur only during

charging. The film products are often mixtures of organic and inorganic lithium compounds. The authors assumed that the reaction occurs at an open circuit potential of 0.4 V vs Li/Li⁺. During charging, the cell voltage rose more quickly to the 4.2 V cutoff (roughly 0.3 hours after 100 cycles, compared to 1.3 hours for the first cycle). Subsequent discharge capacity was less than half the original capacity after 100 cycles. The charging procedure was standard: constant current until 4.2 V followed by constant voltage until the current drops sufficiently (approximately C/100). Increasing the cutoff voltage from 3.9 to 4.2 V resulted in higher overvoltage for the side reaction (more negative voltage than 0.4) and increased resistance. Higher temperatures would increase the rate of the side reaction. These results suggest the need to include a lithium deposition model in future work.

Zhang, Wang, & Tang (2011) cycled graphite-LiFePO₄ (LFP) batteries at 50°C and found that capacity fade came mainly from loss of active Li due the SEI later growth and side reactions.

7.3.3 Copper Dissolution

Copper is typically used as the negative electrode current contactor, since it is relatively stable at normal operating voltages. However, if the negative electrode reaches high voltages, the copper can oxidize and subsequently plate onto the electrode, forming a metallic bridge that could ultimately grow into a short.

Xu, He, Yang, and Xie (2011) examined the failure of an A123 18650 LFP cell under cycling conditions. They found that a 20% overdischarge resulted in failure after eight cycles. The anode potential became quite positive, reaching 4.5 V, which oxidized the Cu contacts at about 3.75 V and reduced it at 3.45 V on the cathode, forming the shorting bridge. However, they were not able to look for lithium plating due to experimental issues, which also was a possible reaction. Zhao et al. (2000) showed that the dissolution process and electrochemical stability depends upon the electrolyte composition.

Because the negative electrode voltage is relatively high for dissolution (3.5 V), large overvoltages with respect to lithium intercalation are required. This suggests that high discharge rates, exceeding the lower cell voltage limit, reduced temperatures, and loss of activity on the anode can be important factors in initiating copper dissolution.

7.3.4 Positive Electrode Dissolution

The positive electrode materials can often react with the electrolyte at operating voltages. Not only is electrolyte decomposition involved, but the positive electrode materials can undergo dissolution, especially at the high voltages near the end of charging and also at elevated temperatures (Balakrishnan, Ramesh, & Kumar, 2006). While this area has been explored for performance fade, less attention has been given to metal plating from dissolution and the relationship to the formation of dendrites and incipient shorts. However, the loss of active species can lead to increased overvoltages for lithium intercalation as well as possible plating conditions, research in both the performance fade and safety categories, and the implications for short initiation, are considered.

Safari and Delacourt (2011) cite a paper that finds Fe dissolution in LiFePO₄ cells, which gave 60 per cent capacity loss in 100 cycles at C/3 rates at 55°C (Amine, Liu, & Belharouak, 2005). Safari and Delacourt summarize the literature on Fe dissolution. Recent study showed that

capacity was primarily reduced by Li-consumption in the SEI layer on the negative (graphite) electrode, which can change the negative electrode overvoltage.

Liu, Kunz, Chen, Tamura, and Richardson (2010) cycled LiFePO_4 batteries from A123 over a wide range of temperatures, depth of discharge (10 to 90%), discharge rates of C/2 to 10C, and charging rates of either C/2 or 2C. The maximum charging voltage was 3.6 V and the minimum discharge voltage was 2.0 V. Measurements of electrode voltage were made with a reference electrode. At no time did the negative electrode's potential become less than zero, suggesting that lithium plating was unlikely for these cells in these conditions, also indicating that the negative electrode capacity in this design exceeded the available active lithium. Iron (Fe) dissolution was observed, but the concentrations were quite low and not a concern. However, there was evidence of breaking and reforming the SEI layer, leading to the loss of active material, which the authors propose to be factors in loss of capacity in their experiments. Increased internal resistance as a result of cycling was not found.

This suggests that lower anode voltages could be found if the anode capacity was less than desired—that is in a cell with insufficient anode graphite interfacial area.

Similarly, Xia, Zhou, and Yoshio (1997) showed that Mn dissolution in spinel cathodes (LiMn_2O_4), phase transition in the positive electrode with dissolution, and electrolyte decomposition were major factors of capacity fade. The fading was faster at 50°C compared to 25°C.

Zhang and Wang (2009) tested high power cycling rates of 5C at 40°C with a $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ positive electrode and a graphite negative electrode. They found that the capacity fade was mainly due to site loss on the positive electrode, resulting in an increase in charge transfer resistance and SEI resistance.

Xu, He, Yang, and Xie (2011) examined the failure of an A123 18650 LiFePO_4 cell under 1C cycling conditions. Capacity faded gradually and internal impedance increased with cycling. The cell failed after 10 cycles with 10% overcharge. With overcharge set to 20%, the cell failed after two to three cycles. Shorting spots were found on the cathode and anode. By using a reference electrode, they determined that the normal charging voltage range was 0.1 to -0.05 V for the negative electrode and 3.0 to 3.90 V for the positive electrode. Overcharge at 110% changed the range: the negative electrode ranged from 0.22 to -0.32 V and the positive electrode from 2.7 to 4.93 V. Upon subsequent discharge, the negative electrode cycled over the same range but the positive electrode ranged from 4.93 V to 2.2 V, yielding a range where oxidation and reduction of Fe is possible. The reactions investigated included the following.

(Oxidation) $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^-$ at 3.70V

(Reduction) $\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$ at 3.25V

(Oxidation) $\text{Fe} \rightarrow \text{Fe}_{2+} + 2\text{e}^-$ at 2.70V

(Reduction) $\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}$ at 2.30V.

In a normal cycle, the authors did not find Fe deposits, but with overcharge they did find deposits. They proposed that Fe oxidized on the positive electrode, and was reduced to Fe metal on the anode and cathode, forming a bridge that initiates the short.

Dissolution of other metals has also been considered, including Mn in LiMn_2O_4 . Wakihara (2001) reported that dissolved Mn was very low in doped LiMn_2O_4 at 50°C. Park, Seo, Plett, Lu, and Sastry (2011) found that capacity fade was higher in LiMn_2O_4 due to dissolved cathode

materials. They found that Mn dissolution was important because of increased contact resistance and loss of active material, with the reaction being $2\text{Mn}^{3+} \rightarrow \text{Mn}^{4+} + \text{Mn}^{2+}$. Mn^{2+} subsequently deposited on the anode. The electrode volume changes due to dissolution were 7 times higher at 50°C than at 20°C. After cycling the battery at C/2 between 3.3 and 4.3 V at 40°C, they found that the capacity decreased 15% at the end of 50 cycles. Jang et al. (1996) found that the manganese dissolution occurred primarily above 4 V, with the capacity fade being due to active material loss and increased contact resistance.

Self-discharge or capacity fade with calendar time, as opposed to fade due to cycling, is also important for reducing the active lithium for participating in intercalation. This loss of active material can possibly lead to increased overvoltages, which may lead to undesired side reactions.

7.3.5 Effect of Temperature

Slower kinetics at low temperature can lead to plating on the negative electrode, particularly at high charging rates (Bandhauer, Garimella, & Fuller, 2011). In addition, capacity fade may be higher at higher temperatures; a summary of recent research is given in Bandhauer, Garimella, and Fuller (2011). They cited mechanisms that included dissolution of Fe^{2+} (with a sensitivity to electrolyte), loss of lithium to the SEI layer, sensitivity to maximum voltage, and insensitivity to depth of discharge for capacity and energy, but not power. In one cited study, power fade was dependent upon both time and temperature after an initial period of four weeks. However, Zhang, Wang, and Tang (2011) found increased capacity and power fade at lower temperatures, primarily due to the loss of active lithium to the SEI layer. Similarly, Svensson (2011) reported a 40% loss of the capacity at 10°C, compared to 24°C data. Loss factors included increased resistance to solid diffusion of lithium, increased electrolyte resistance, and increased SEI layer resistance.

Thermal runaway and the exothermic reaction sequence, as a function of temperature, was discussed extensively in Chapter 2. As noted, thermal runaway occurs when the rate of heat generation exceeds the rate of heat dissipation, and this is dependent not only on the heat generating reactions, but on the thermal design of the batteries. The methods of cycling can also increase the temperature substantially (Bandhauer, Garimella, & Fuller, 2011). Detecting the rise in temperature due to shorting in sufficient time for control action is difficult, because the early stage of a short is such a local event (Keyser et al., 2011). The thermal design of Li-ion batteries has been extensively studied by Pesaran's group at NREL.

7.3.6 Summary

Mechanistic understanding should be considered incomplete. Table 7-1 presents a summary of the main points, from the papers cited above, that have implications to the effect of driving cycle on the growth of internal shorts. This is somewhat simplified, because of the variety of chemistries and operating conditions, as well as the limited studies, so this should be considered a general overview.

Table 7-1. Summary of factors that accelerate loss mechanisms (preliminary).

Loss	Potential	Charging	Discharging	T	Aged Cell	Mechanism Origin
Lithium plating	$E \leq 0V$	High rates, overcharge		Worse at low T	Worse	Plated on negative electrode. Worse with mismatched capacities and sensitive to voltage nonuniformity.
SEI decomposition	0.4 V ^a has been used, although more research is needed.	High rates during constant voltage stage of charging				Often on negative electrode, but growth of SEI layer resistance on positive electrode has been mentioned.
Copper support dissolution	3.5 V ^b		High rates and overdischarge	Worse at low T	Worse after cycling	Oxidized on negative, reduced on positive electrode
Cathode dissolution	Fe 2.3 -3.7 V ^b Mn: > 4.0 V ^c	High rates, overcharge	High rates, overdischarge	Capacity fade can be larger at higher T	Capacity loss after cycling	Positive electrode, but may be reduced on negative electrode. Expected to be sensitive to voltage nonuniformity.

^a Ramadass, Haran, Gomadam, White, & Popov (2004)

^b Xu, He, Yang, & Xie (2011)

^c Park, Seo, Plett, Lu, & Sastry (2011)

Typically, these losses are higher with aged, cycled cells, although that is not always true. Generally, mismatched capacities between anode and cathode can polarize one side excessively under high or low states of charge and could accelerate failures if the polarized electrode is pushed into a voltage range for the side reaction.

7.4 Lithium-ion Battery Model

Modeling was performed to assess and illustrate the influence of a variety of operating conditions, including calculations representative of both new and aged batteries, on initiation and growth of potentially damaging side reactions. To model the Li-ion battery system, we used the Newman model (Fuller, Doyle, & Newman, 1994), which is a widely used, essentially one-dimensional model that has been validated for a number of cases. In many applications of this model, the Butler-Volmer reaction equations are linearized, which speeds up numerical solution of the equations. However, the present focus was on cases where the overvoltage is high and the linearization approximation is not valid. Consequently, the Comsol 3.5a (Comsol AB, Stockholm, Sweden) implementation of the Newman model was used, which retains the full nonlinear form and can still solve the equations rapidly. The Comsol model is also widely used, with recent examples being Chandrasekaran and Drews (2011), Wang and Sastry (2007), Cai and White (2009), Tang, Albertus, and Newman (2009), and Bernardi and Chandrasekaran (2011).

The Comsol implementation of the Newman model uses one-dimensional equations for the voltage and the lithium concentration in the electrolyte. The particulate phases in both electrodes are modeled as an assembly of spheres with the lithium diffusion within the spheres described by one-dimensional equations. The voltage equation is quasi-steady in time, while the diffusion

equations are unsteady. The nonlinear form of the Butler-Volmer equations are used to describe the electrochemical reactions at the electrode-electrolyte interfaces.

The Li-ion battery model in Comsol version 3.5a was used for the calculations. Ten elements were used for both negative and positive electrodes, and 15 elements were used in the separator for the one-dimensional electrolyte phase calculations. The solid phases were represented by 88 and 78 elements for the negative and positive electrodes, respectively.

The model solved the equations rapidly and was relatively robust in the charging mode. With discharge calculations, convergence could sometimes be difficult near the upper and lower cutoff voltages, limiting our ability to estimate the time in these unsafe conditions. Consequently, we combine our modeling efforts with literature results to illustrate the conditions that may accelerate the formation of internal shorts and to suggest areas for additional research. The numerical issues may not be a fundamental limitation, since extensive work has been done on modeling these systems and more advanced implementations of the Comsol model are available.

Other advanced models are under development. Witzelhausen, Käbitz, and Sauer (2012) modeled the charge and temperature distribution within an 18650 size cell. They compared model results with measurements and simulated a short circuit internal to a cell in a larger battery pack. Nieto et al. (2013) measured the heat distribution in a 10.5-Ah pouch cell, considered the mechanisms involved, and developed a model for the heat generation. Their goal was to design an improved battery thermal management system. Gerver and Meyers (2011) developed a model of the thermal and electrochemical behavior in a cell, including both three-dimensional spatial distribution and transient effects. Gerschler, Kirchhoff, Witzelhausen, Hust, and Sauer (2009) modeled the mechanical stress as well as the electrochemical and thermal behavior of a 6-Ah prismatic pouch cell, and studied the behavior of packs of cells over their entire life cycle. Kim, Smith, Lee, and Santhanagopalan (2011b) recently examined dendrite formation in large batteries in overcharge situations. The growth is a function of local geometry and occurs at specific weak points. The National Renewable Energy Laboratory (NREL) started with a scanning electron microscope image of local porosity and generated a mesh from that. Future work includes cathode volumetric changes during overcharge, and electrolyte decomposition. Investigators have made it clear that there is a need for better models describing side reactions, such as the growth of the SEI layer (Ramadesigan, Northrop, De, Santhanagopalan, Braatz, & Subramanian, 2011).

7.5 Simulation Results

To examine these literature results further, we present example calculations of the electrode potentials at a variety of operating conditions, including calculations representative of both new and aged batteries. The calculations are designed to illustrate the phenomena discussed above, but should not be considered a definitive calculation of a particular failure or cycling scenario. Furthermore, there are a wide variety of battery chemistries, designs, and operating conditions, and so we expect a wide range of behaviors. Here we seek some general illustrations of the importance of common effects in the charging and discharging protocols.

For these examples, we use a graphite negative electrode with a LiMn_2O_4 positive electrode. The electrolyte is representative of 1:2 EC:DMC with LiPF_6 as the salt. The Newman battery model has been validated against data for this particular battery and we chose to use the same dimensions and material properties used for that validation paper (Doyle, Newman, Gozdz,

Schultz, & Tarascan, 1996) and in the formulation developed by Comsol. In these calculations, we treat the battery as being at room temperature.

The battery properties are summarized in Table 7-2.

Table 7-2. Li-ion battery used in calculations.

Negative electrode	Graphite
Positive electrode	LiMn ₂ O ₄
Electrolyte	1:2 EC:DMC with LiPF ₆
Negative electrode width	100 microns
Positive electrode width	183 microns
Separator width	52 microns

In evaluating this battery, Doyle, Newman, Gozdz, Schultz, and Tarascan (1996) state that the positive electrode has 41% excess capacity. The model was run in both charging and discharging conditions. For charging, a constant voltage was used to a specified cutoff, which in normal operation was 4.2 V. For discharging, a constant current was used to a specified lower voltage limit, normally 2.7 V.

7.5.1 Open Circuit Potential and Loss Ranges

The open circuit voltage is a function of the species concentrations and the temperature. Figure 7-1 shows the open circuit potential for the positive and negative electrodes at room temperature as a function of the SOC, which is defined as the surface concentration of lithium divided by the maximum concentration possible in the particle.

Lithium plates onto the negative electrode when the electrode voltage is less than zero, and the figure shows that the potential approaches zero at SOC \approx 0.7. During charging, the electrode voltage will be reduced further, particularly as the lithium sites become filled, so the voltage will approach zero at a SOC $<$ 0.7 and can become significantly negative. Thus, to plate lithium, large overvoltages are required at low SOC's, and small overvoltages are required at high SOC's. The charging window is designed to keep the SOC within the safe range, to avoid lithium plating and other side reactions.

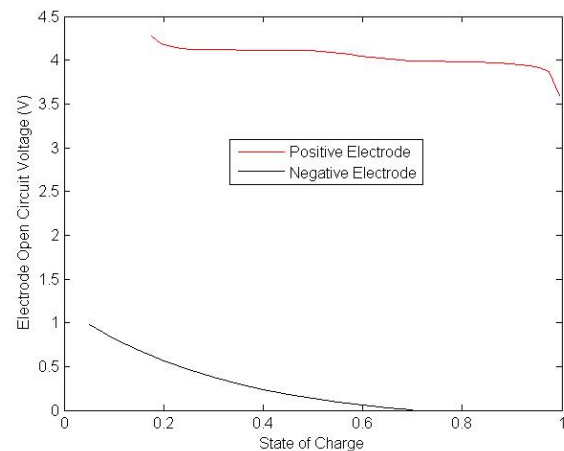


Figure 7-1. Open circuit potential for positive and negative electrodes.

7.5.2 . Charging Results

Charging calculations were run at three charging rates, 0.5C, 1C, and 2C, for both new and degraded batteries. Normal operation was to charge the cells to 4.2 V. The initial SOC was 0.23 and 0.55 for negative and positive electrodes, respectively. Figure 7-2 shows the charging curves for the new battery at a 1C rate. Figures 7-3 and 7-4 show the charging curves at 0.5 C and 2 C rates.

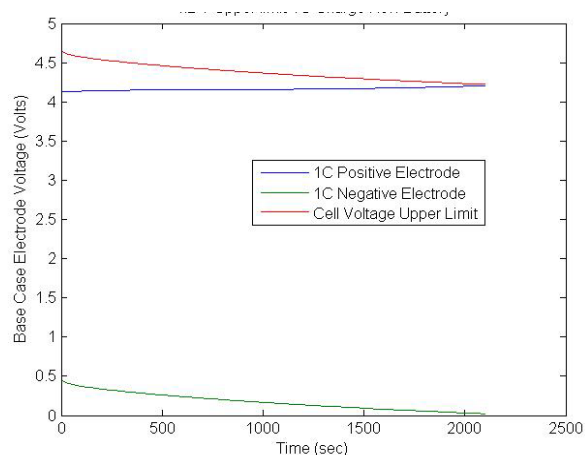


Figure 7-2. Positive and negative electrode voltages at the separator interfaces for a charging rate of 1 C.

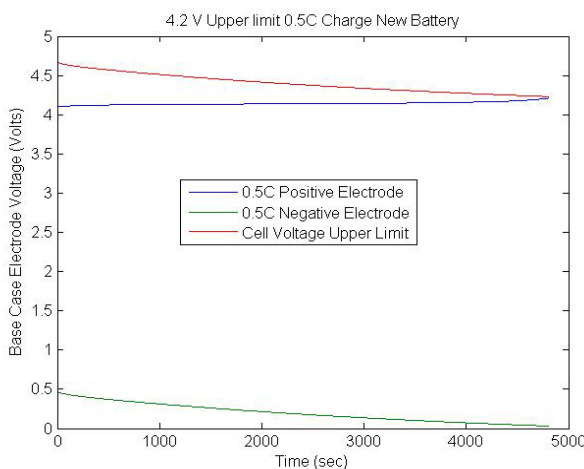


Figure 7-3. Positive and negative electrode voltages at the separator interfaces for a charging rate of 0.5 C

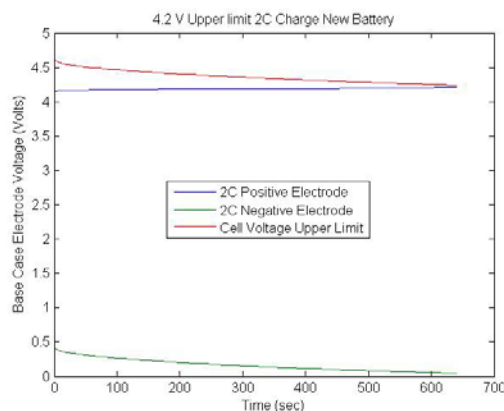


Figure 7-4. Positive and negative electrode voltages at the separator interfaces for a charging rate of 2 C

Figures 7-2, 7-3, and 7-4 show the voltage at the negative-electrode separator interface and the positive- separator interface, since the overvoltage is highest at these locations. Also shown is the cell voltage limit, which we assumed to be a cell voltage difference of 4.2 V. Since the open circuit voltage is also 4.2 V and the positive electrode voltage is nearly constant with time, the cell voltage limit is not reached until the negative electrode voltage reaches 0 V. Thus the negative electrode voltage remains greater than or equal to zero at all times until the cutoff. In fact, we generally expect this to be true, since E_p should increase with time during charging and E_n should decrease with time, and the voltage cutoff of 4.2 will keep $E_{cell} \geq 0$ at all times.

Next, we consider an aged battery that has degraded due to cycling or calendar life. In this case, we assume that both the exchange current density (a measure of reaction rate: see Equation 7-2 above) and the lithium diffusivity in the electrolyte have degraded to 25% of the original values. Furthermore, we assume that the overcharge limit failed and the cell charges to 4.5 volts. Figure 7-5 shows voltages on the positive and negative electrodes, along with the cutoff voltage for a charging rate of 1 C. Here the lower electrode voltage becomes negative at 1460 seconds, while the cell voltage is 4.19 V. With the voltage cutoff limit in failure, the negative electrode voltage decreases to -0.139 V, where lithium plating is expected to occur. Furthermore, we have not considered the change in open circuit voltage as a battery ages. Typically this voltage will decrease with age and consequently a cell cutoff voltage of 4.2 volts may allow one of the electrodes to overcharge. Thus, the charging algorithm needs to use the actual open circuit voltage, including its change over time.

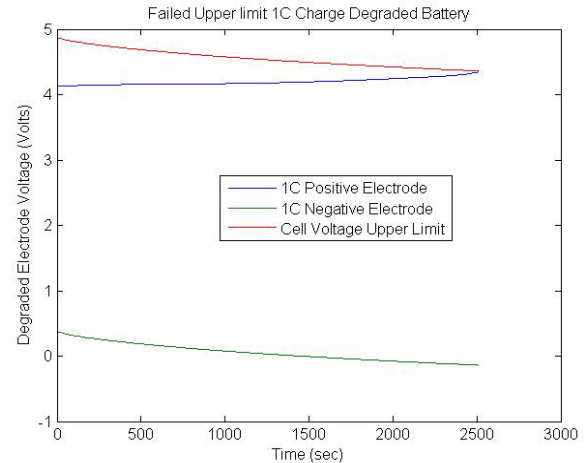


Figure 7-5. Degraded battery: positive and negative electrode voltages at the separator interfaces for a charging rate of 1 C.

7.5.3 Discharging Results

Next we consider the discharge case using the new and degraded batteries. For the degraded batteries, we considered two conditions: (1) a resistive layer on the negative electrode with a fixed voltage loss of 0.18V, representative of a thickened SEI layer, and (2) the same resistive layer plus the exchange current density and the electrolyte diffusivity degraded to 0.25 of the new values. The batteries were discharged at constant currents of 1C and 3C. Initial state of charge was 0.56 and 0.17 on the negative and positive electrodes, respectively, which represents a fully charged battery with an open circuit voltage of 4.22 V. The discharge curves (Figures 7-6 and 7-7) show a more rapid discharge in the 3C case than the 1C case and the effect of each degradation case can be clearly seen

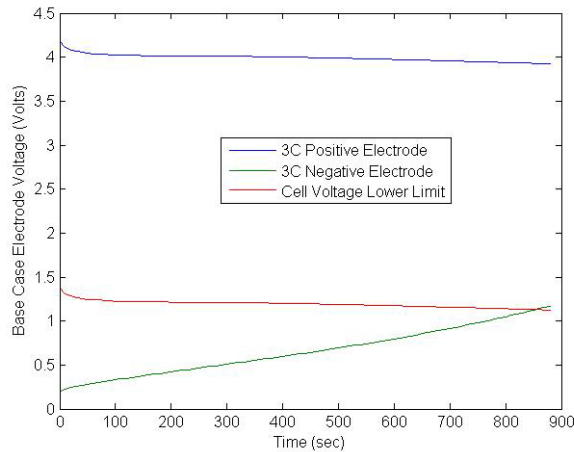


Figure 7-6. Negative and positive electrode voltage at the separator interface for a new battery at 3 C.

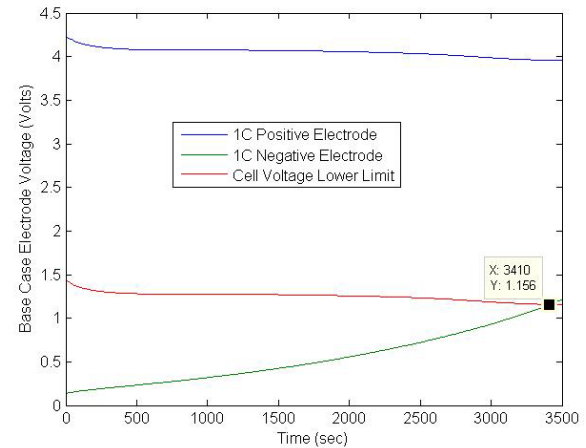


Figure 7-7. Negative and positive electrode voltage at the separator interface for a new battery at 1 C.

There is no change on the maximum negative electrode voltage because the cathode curve is relatively flat. Subtracting the lower voltage limit gives the red curve shown in Figures 7-8 and 7-9. The cell shuts down when the anodic overvoltage reaches the cutoff limit. Since that limit is nearly flat, the anodic voltage never rises much above 1.2 V. The maximum anode voltage is then the open circuit voltage minus the lower limit or about $4.2 - 2.8 = 1.4$ V.

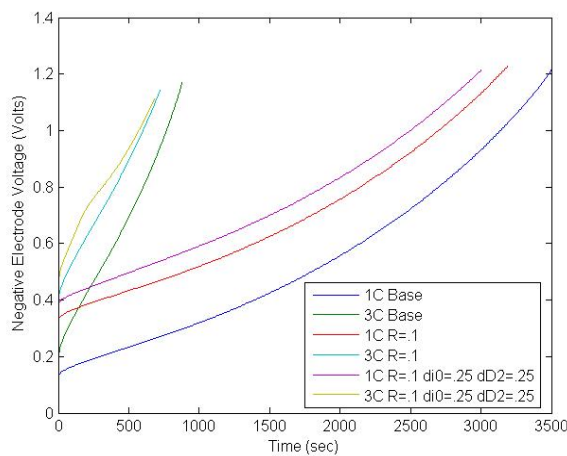


Figure 7-8. Negative electrode voltage at the separator interface for new and aged batteries at discharging rates of 1 C and 3 C.

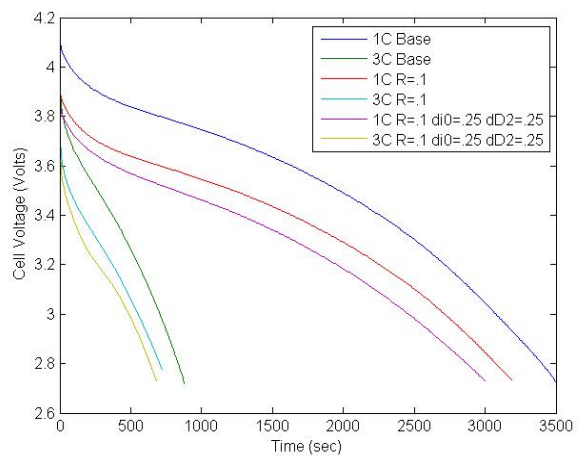


Figure 7-9. Cell voltage for new and aged batteries at discharging rates of 1 C and 3 C.

Similar results would be obtained by plotting the degraded curves. If the cathode is degraded, the lower limit curve moves down and the anodic overvoltage is less positive. If the lower limit control fails, however, the anodic overvoltage can climb higher. Unfortunately, the software generally will not converge during those conditions and the model was unable to compute the maximum rise in voltage. Xu (2011) showed that in overdischarge conditions the anodic voltage could exceed 3.5 V, where the copper support layer could dissolve and plate onto the cathode.

Next we consider a 10C discharge with a failed lower voltage limit and a degraded battery (Figure 7-10). The program ran into numerical difficulties once the cathode voltage began to drop rapidly, but the plot shows that the anode voltage reached 1.8 V when the cell voltage was 1.645 V. This is well below the copper dissolution condition of 3.75 V on the negative electrode. However, we note that Xu, He, Yang, and Xie (2011) provided experimental evidence of high negative electrode voltages and copper dissolution, suggesting that the model does not capture the phenomena at high anodic voltages.

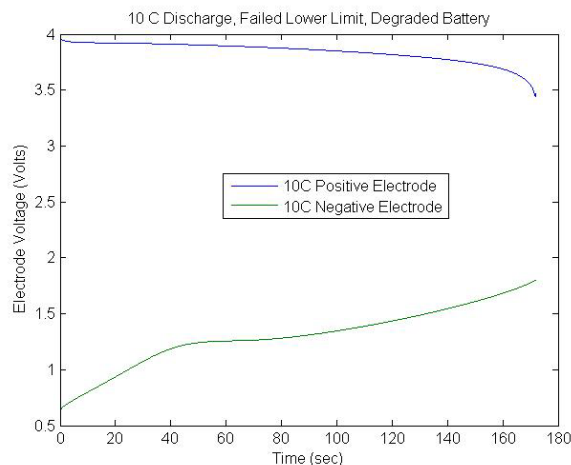


Figure 7-10. Negative and positive electrode voltage at the separator interface for an aged battery at 10 C.

7.6 Operating Conditions and Driving Cycle Implications

The acceleration of internal short circuiting is receiving much attention in the research community, but the mechanisms are not fully clarified. It is clear however, that many electrodes and electrolytes are not stable over the full voltage range of the battery during charge and discharge cycles. This becomes worse if the operating voltage is extended by failure of the monitoring and control circuits, allowing the voltage to be outside the normal range. This is further complicated by the difficulty in predicting individual electrode voltages from cell voltage measurement, the variations in cell-to-cell voltage, and the need for high charging and discharging rates in vehicle batteries. These out of range voltage excursions can lead to the undesired side reactions discussed in this chapter. From a study of the literature and the modeling examples, we conclude the following.

In the calculations, the cell limits worked well in normal operating conditions and kept the electrodes within acceptable voltage ranges. However, when the voltage limits failed and the cell was allowed to overcharge or overdischarge, the electrode voltages reached levels of concern, particularly for lithium plating on charging. There is direct experimental evidence from the work of Xu, He, Yang, and Xie (2011) that both overdischarging and overcharging can lead to electrode voltages that cause electrode and support dissolution.

Our calculations were one-dimensional, which can illustrate many of the changes of voltage on each electrode. However, Tang, Albertus, and Newman (2009) showed that voltage nonuniformities of up to 1 V could arise on the electrodes they modeled, resulting in the positive electrode reaching considerably higher voltages than allowed. Consequently, some failure modes are at least two-dimensional and dependent upon the detailed geometry.

Both low and high temperatures can influence battery side reactions. Low temperatures increase the charge transfer resistance and degrade the transport properties, which in turn increase the intercalation overvoltage. High temperatures can increase capacity fade and the tendency for side reactions to occur.

Consequently, cells may undergo undesirable side reactions that could initiate plating. This in turn could lead to internal shorting when cell voltages are limited to cutoff voltages corresponding to normal full charge under the following circumstances:

- Cell voltage nonuniformities that allow one region of the electrode to differ significantly from the average or measured value of voltage
- Decrease in capacity or open circuit voltage of at least one of the electrodes, or mismatched capacity in the battery design, that allows the other electrode to reach an out of range condition while the cell voltage is in the acceptable range.

In addition, cells may also undergo undesirable side reactions when the voltage, current, or temperature limiting circuitry or measurements fail and the cell is allowed to overcharge or overdischarge. These effects are made worse and occur in shorter times under the following circumstances.

- Resistance to charge transfer that is increased by resistive layers forming on the electrodes due to side reactions
- Low temperatures that increase charge transfer resistance
- High charging rates
- High discharging rates
- Imbalanced electrode capacities, which unduly polarize one electrode
- Contamination or poisoning of catalyst layers
- Capacity or power fading during cycling due to loss of active material and degraded transport properties
- High temperature that accelerates capacity fading.

Consequently, testing and driving cycles for Li-ion batteries to evaluate safety should include:

- Rates that exceed the highest and lowest charging and discharging rates that are expected in operation.
- Rates that include temperatures that exceed the highest and lowest operating temperatures of the battery, both in normal operation and in modes of abnormal temperature control.
- Aged as well as new batteries, since cycling can increase the charge transfer resistances and change the properties, including the open circuit voltage and the amount of active lithium in the battery.
- Methods to measure or predict the voltage of each electrode. This should be considered during the design of testing cycles and possibly during testing. It may be possible to use models fit to the battery performance to determine the testing conditions that would push the individual electrodes to extreme values where side reactions occur.
- Methods to diagnose the initiation of plating, which can lead to internal shorts. These methods need to be developed to evaluate the results of safety testing. With cell failure rates of 1 in 10^6 and long times required for plated dendrites to grow into a short, it may

be challenging to assess the outcome of testing. It is not clear how to define or measure an acceptable growth rate for plating in testing conditions.

- Further advancement of the current state of modeling and of characterizing side reactions related to internal short circuiting. This may ultimately be used to help diagnose incipient shorting.

7.7 Areas for Future Research

Side reactions and internal short circuiting in batteries is an active field of research now, as evidenced by the numerous talks at the October 2011 Electrochemistry Society Meeting in Boston in the reference list below (Bernardi & Chandrasekaran; Kim, Smith, & Pesaran; Ofer, McCoy, Barnett, & Sriramulu; Orendorff; Ramadesigan, Northrop, De, Santhanagopalan, Braatz, & Subramanian; Svensson; Xu, He, Yang, & Xie). Major progress has been made in modeling techniques, validation, and experimental approaches. Dissolution of electrode materials is getting significant attention, especially related to internal shorts and capacity fade. However, many question still remain, in particular the issues related to the diversity of battery chemistries and designs. Below are suggestions for consideration on the areas for future research based upon our review of selected technical literature and on battery simulations:

- Better quantitative understanding of operating conditions and mechanisms associated with electrode dissolution, electrolyte breakdown, resistive layer growth and reforming, and lithium plating.
- Better quantitative understanding of the relationship between the above phenomena and the tendency to form incipient short circuits and dendritic growth.
- Robust modeling at high overvoltages representative of reactions outside the usual safe operating window.
- Experimental and modeling techniques to diagnose the formation of incipient shorting in Li-ion batteries. As inputs, these techniques should use commonly measured data, such as cell voltage, current, and temperature at select locations.
- Experimental and modeling techniques that can be used to develop testing cycles that accelerate realistic shorting conditions. This includes identifying the specific charging and discharging waveforms that create the conditions where plating is expected to occur for a specific battery chemistry.

7.8 References

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8 Overview of Relevant Safety Standards

This chapter presents summary-level information on standards promulgated by seven organizations, such as the Society for Automotive Engineers, the International Organization for Standardization), Underwriters Laboratories, and the Institute for Electrical and Electronics Engineers, applicable to Li-ion batteries, with a focus on safety standards as Li-ion systems are deployed in vehicles. The section documents the tests that battery systems must undergo to pass various standards, including the method of test, the conditions, and the outcomes required. Examples of the standard test types include vibration, thermal shock, electrical short circuit, immersion, crash and drop tests, overcharge, and cell aging.

Battery manufacturers and manufacturers of battery-powered products design products to deliver specified performance characteristics in a safe manner under anticipated usage conditions. As such, failure (in either performance or safety) can be caused by poor design, or an unexpected use or abuse of a product. Active or passive safeguards can be designed to mitigate or prevent some failures. But given the ever-changing chemistry of Li-ion cell designs, not all safeguards will work including those designed to preserve the thermal stability of active materials within the battery at high temperatures and those designed to prevent internal short circuits that may lead to thermal runaway. Understanding potential failure modes is still emerging as this complex technology continues to advance to meet demands.

A number of standards and testing guidelines have been developed to provide battery manufacturers and users with direction on how to more safely construct and use Li-ion batteries. These standards and testing protocols incorporate a number of product safety tests designed to evaluate a battery's ability to withstand certain types of abuse or specific risks from electrical, mechanical, and environmental conditions. The most relevant safety standards for this project are those promulgated by SAE, the United Nations Economic Commission for Europe, UL, IEEE, and Sandia National Laboratories for the FreedomCAR program (Doughty & Crafts (2006).

The SAE Recommended Practice J2464 and the Sandia "Abuse Test Manual" simulate use and abuse (mechanical, thermal and electrical) beyond the normal safe operating limits observed in electric and hybrid electric vehicles. SAE J2929 focuses on lithium-based rechargeable battery systems intended for high-voltage applications. UL 2580 provides test methods for Li-ion battery packs, subassemblies and modules to be used in vehicles. It leverages test methods from J2464.

The U.N. Test Methods and Criteria (Section 38.3) gives procedures for testing and classifying lithium metal and Li-ion cells and batteries under conditions simulating various altitude, thermal, vibration, shock, short circuit, impact, overcharge, and forced discharge conditions. U.N. 38.3 (2010) includes the following two definitions.

- *Large battery* means a lithium metal battery or Li-ion battery with a gross mass of more than 12 kg.
- *Large cell* means a lithium metal cell in which the lithium content of the anode, when fully charged, is more than 12 g, or in the case of a Li-ion cell, means a cell with a Watt-hour rating of more than 150 Wh.

Corresponding definitions for small battery and small cell are below these limits. The standard specifies different test procedures for large and small batteries. Section 38.3.3 calls for fewer

rechargeable large batteries to be tested and after fewer cycles, than comparable tests for small batteries, in the tests other than the impact and forced discharge tests. Two of the tests themselves are different. The dwell time at extreme temperatures in the thermal test (T2) is at least 12 hours for large cells and batteries, instead of the 6 for small batteries. The shock pulse (T4) for large cells and batteries is less amplitude but longer duration for large cells and batteries (half sine at 50 g and 11 ms for large instead of 150 g and 6 ms). Neither the manual itself nor the proposal leading to its revision (PRBA, 2008) gives a rationale for the differences in requirements.

The UL Standard 1642 is intended to reduce the risk of fire or explosion when technician- or user-replaceable, lithium-based batteries are used in a product, or when such batteries are removed from a product and discarded. The IEEE standard 1725 provides criteria for qualification, quality, and reliability of rechargeable Li-ion and Li-ion polymer batteries for cellular telephone applications. The standard also covers battery pack electrical and mechanical construction, packaging technologies, pack and cell level charge and discharge controls, and overall system considerations. Taken together, these standards, criteria, and practices provide a wide range of guidelines on design and laboratory testing considerations to help ensure the safety of Li-ion batteries in vehicles (Tables 8-1 and 8-2).

Similarly named test procedures in various documents might not be executed using the same specifications or methods. For example, there may be variations between documents regarding the number of samples required for a specific test, or the electrical characteristics prior to testing (Table 8-1).

Table 8-1. List of safety standards of Li-ion batteries.

Organization	Designation	Title	Year	Applicability	Summarized in this Chapter
Sandia Report	SAND2005-3123	FreedomCAR Electrical Energy Storage System Abuse Test Manual for Electric and Hybrid Electric Vehicle Applications (Doughty and Crafts 2006)	2006	Cell, module, or pack in a motor vehicle	
SAE International	SAE J2464	Electric and Hybrid Electric Vehicle Rechargeable Energy Storage Systems (RESS), Safety and Abuse Testing	2009	Cell, module, or pack in a motor vehicle	Table 8-4
	SAE J2929	Electric and Hybrid Vehicle Propulsion Battery System Safety Standard — Lithium-Based Rechargeable Cells	2011	System or whole vehicle	Table 8-3
International Organization for Standardization	ISO 6469-1	Electrically propelled road vehicles -- Safety specifications – Part 1: On-board rechargeable energy storage system (RESS)	2009	Cell, module, or pack in a motor vehicle	
	ISO 6469-2	Electrically propelled road vehicles -- Safety specifications – Part 2: Vehicle operational safety means and protection against failures	2009	System or whole vehicle	
Underwriters Laboratories	UL 1642	Standard for Lithium Batteries	2005		Table 8-6
	UL 2580	Batteries for Use in Electric Vehicles	2011	Packs, subassemblies and modules in a motor vehicle	Table 8-7
International Electrotechnical Commission	IEC 62133	Secondary Cells and Batteries Containing Alkaline or Other Non-acid Electrolytes — Safety Requirements for Portable Sealed Secondary Cells, and for Batteries Made from Them, for Use in Portable Applications	2002		
	IEC 62281	Safety of Primary and Secondary Lithium Cells and Batteries during Transport	2004	For transporting batteries	
United Nations	38.3 (E.09.VIII.3)	Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, Part III, Section 38.3	2010	For transporting batteries	Table 8-5
Institute of Electrical and Electronics Engineers	IEEE 1625	Rechargeable Batteries for Multi-Cell Mobile Computing Devices	2008	Not to vehicles	
	IEEE 1725	Rechargeable Batteries for Cellular Telephones	2011	Not to vehicles	Table 8-8

Table 8-2. Summary of the standards that are specific to vehicles.

Nature of the Test		Freedom Car (2006)				SAE J2929 (2011)		UL 2580 (2011)		SAE J2464 (2009)				UN 38.3 (2010)			Comments
			Cell	Mod	Pack		system (or vehicle) level		Packs or Subassemblies		Cell	Mod	Pack		Cell	Battery	
Mechanical	Mechanical Shock	3.6	--	3 levels		4.5	system: UN or J2464; vehicle FMVSS 305	24	J2464 shock test	4.3.1	UN	--	25 g	T4	150 g or 50 g X 18 shocks		All differ.
	Drop	3.3	--	--	10 m to a pole	4.3	J2464	25	1 m to a flat surface	4.3.2	--	--	2 m to a flat	T6	weight on rod across DUT	--	All differ. UN is a cell test; others are pack tests. DUT=device under test.
	Penetration	3.2	pointy steel 8 cm/s							4.3.3	pointy steel 8 cm/s						Freedom Car and J2464 essentially identical
	Roll-Over	3.5	--	1 rpm, 4 60-min holds				22	Rotation 3 axes	4.3.4	--	1 rpm, 4 60-min holds					Freedom Car and J2464 essentially identical
	Immersion	3.4	minimum 2 hr 25 C salt			4.4	J2464	29	J2464	4.3.5	minimum 2 hr salt						Freedom Car specifies temp, J2464 more specific on salinity
	Mechanical Integrity	3.1	--	crush on cylinders		4.6	J2464 or FMVSS 305	26	Crush 3 axes	4.3.6	special fixture	crush on cylinders					J2464 has a cell test; Freedom Car does not.
	Vibration					4.2.2	UN, J2380, or custom	23	Anticipated profile or J2380					T3	frequency sweep		J2929 gives several choices.
Thermal	Fire Exposure	4.2	--	radiant 890 C		4.7	pick a fire	30	Fire and projectile test	4.4.1	--	radiant 890 C					J2464 is more detailed.
	Thermal Stability									4.4.2	ramp, 30-min holds	--	--				
	High Temperature Storage	4.3	2 months, sampled														Freedom Car is the only standard with this test.
	Cycle w/o Thermal Control	4.4	20 cycles			4.11	J2464	21	Max charge and discharge w/o cooling	4.4.3	20 cycles & wait						J2464 is more detailed.
	Cycle w/Thermal Control							16	Max charge and discharge, 10 cycles								
	Thermal Shock	4.5	50% SOC			4.2.3	UN or J2464	27	J2464 from 85°C to -40°C	4.4.4	100% SOC			T2	10 cycles		Differ in SOC, temp, number of cycles
	Humidity Exposure					4.2.4	IEC										J2929 cites IEC
	Passive Propagation							31	J2464	4.4.5	--	heat one cell					J2464 is the only standard with this test.
	Electrical	Short Circuit	5.2	--	hard for 10 min		4.8	UN or 4.5.1	14	hard short	4.5.1	soft or hard short			T5	test warm	

	Overcharge	5.1	--	1 of 3 tests		4.9	normal charge, control disabled	13	Max charge rate, single fault in charge circuit	4.5.2	cells and module+pack differ			T7	2X current		Criteria and procedures all differ.
	Overdischarge	5.3	--	overdischarge, reversal separate				15	Discharge until protections activate	4.5.3	current	battery		T8	12 V DC		All differ.
	Separator Shutdown									4.5.4	heat then overvolt	--	--				J2464 is the only standard with this test.
	High Voltage Exposure					4.13	auto and manual	18	Test for dielectric breakdown								J2929 is the only.
	Partial Short Circuit	5.4	--	hard short some central units													FreedomCAR is the only standard with this test.
	Imbalanced Charging							17	Charging unbalanced modules								
	Isolation Resistance							19	Electrical isolation/ shock hazard								
	Continuity Test							20	Continuity of grounding system								
Other	Hazardous Substance									4.2.1	Four tests: electrolyte saturation, cell abuse short of runaway, cell with runaway, and pack level abuse						
	Salt Spray Immersion							28	Marine environment and road salt test								
	Altitude Simulation													T1	6 hours at 11.6 kPa		

8.1 *Electric and Hybrid Vehicle Propulsion Battery System Safety Standard – Lithium-Based Rechargeable Cells, SAE J2929 (2011)*

Scope: Battery System includes components to implement complete functional energy storage system including battery packs and necessary ancillary subsystems for physical support and enclosure, thermal management, and electronic control (Table 8-3).

Table 8-3. Summary of the vehicle-level tests in SAE J2929.

Tests	Description	Conditions	Required Outcome
4.4.2 Vibration			
(Alternative 1: Complete battery system test)	Complete battery system tested in accordance with one of: 1. U.N. Test Manual, Test T.3 vibration profile, 2. SAE J2380 vibration profile, 3. Custom profile from the responsible organization reflecting the actual application.	If SAE J2380 selected, state of charge shall be at maximum possible during normal vehicle operation throughout test.	1. No fire or explosion during the test or for an hour afterward. 2. High voltage to ground isolation of at least 100 Ω/V (measured IAW ISO 6469-1, Sect. 6.1.3). 3. Post-test pack open circuit voltage at least 90% of pre-test voltage. 4. No cracking or loosening on visual inspection.
(Alternative 2: Battery subsystem test) Part A & B required	Part A – Components or subsystems of the battery system tested in accordance with one of: 1. U.N. Test Manual, Test T.3 vibration profile, 2. SAE J2380 vibration profile, 3. Custom profile from the responsible organization reflecting the actual application.	Selection of components or subsystem left to the decision of the tester.	No fire or explosion during the test or for an hour afterward
	Part B – Complete battery system shall be tested as part of a vehicle-level vibration test where the battery system is subject to conditions appropriate to the vehicle's operation. Vibration profile shall be specified by the responsible organization.	The battery state of charge and temperature shall be that of normal vehicle operation for the ambient conditions during the vehicle test and shall not be artificially restricted.	1. From before the test begins to the conclusion of a 1 hour post-test observation period, no enclosure rupture, fire, explosion, or venting shall occur. 2. High voltage to ground isolation of at least 100 Ω/V shall be maintained (measured IAW ISO 6469-1, Sect. 6.1.3 or equivalent). 3. Post-test pack open circuit voltage shall be no less than 90% of pre-test pack open circuit voltage. 4. Visual inspection of battery system internal components shall identify no evidence of cracked, damaged, or loosened high-voltage conductors which are part of the primary power current path.

Tests	Description	Conditions	Required Outcome
4.2.3 Thermal Shock			
	Simulates a rapid temperature change environment which a battery system will likely experience during its life.	Complete battery system is to be tested IAW either U.N. Test Manual T.2, or the thermal shock profile defined in SAE J2464, Section 4.4.4. Note that while battery modules or sections may be individually tested IAW U.N. requirements, a complete battery system is to be tested for this condition, except as allowed by per 4.1.3 of J2929.	<ol style="list-style-type: none"> 1. From before the test begins to the conclusion of a 1 hour post-test observation period, no enclosure rupture, fire, explosion, or venting shall occur. 2. High voltage to ground isolation of at least 100 Ω/V shall be maintained (measured IAW ISO 6469-1, Sect. 6.1.3 or equivalent). 3. Post-test pack open circuit voltage shall be no less than 90% of pre-test pack open circuit voltage. 4. Visual inspection of battery system internal components shall identify no evidence of cracked, damaged, or loosened high-voltage conductors which are part of the primary power current path.
4.2.4 Humidity/Moisture Exposure			
	Simulates a temperature and humidity environment which a battery system will likely experience during its life.	Tested IAW IEC 60068-2-30 with a severity of 55°C with 6 cycles, using Variant 1 during the temperature lowering period.	<ol style="list-style-type: none"> 1. From before the test begins to the conclusion of a defined recovery period, no enclosure rupture, fire, explosion, or venting shall occur. 2. High voltage to ground isolation of at least 100 Ω/V shall be maintained (measured IAW ISO 6469-1, Sect. 6.1.3 or equivalent). 3. Post-test pack open circuit voltage shall be no less than 90% of pre-test pack open circuit voltage. 4. Visual inspection of battery system internal components shall identify no evidence of cracked, damaged, or loosened high-voltage conductors which are part of the primary power current path.

Tests	Description	Conditions	Required Outcome
4.3 Drop Test			
	Simulates a service condition where the battery system is removed (or being removed) from the vehicle and is dropped while separate from the vehicle.	<p>Complete battery system tested IAW SAE J2464, Sect. 4.3.2, with following exceptions:</p> <ol style="list-style-type: none"> 1. Drop surface shall be integral and massive enough to be immovable. 2. Surface shall be horizontally flat and rigid enough to be non-deformable. 3. Surface shall be large enough that the battery system falls entirely upon the surface. 4. Battery system oriented to represent most likely impact orientation (responsible organization shall document rationale, and if most likely is flat, second most likely shall be used). 5. State of charge shall be maximum level for service situations, if different than the maximum possible during normal vehicle operation which normally applies. 6. If battery removal requires attachment of tool/fixture, it may be included in drop test. 7. Drop height shall be max distance to ground that battery system experiences when serviced according to documented procedures, but not less than 1 m. 	<ol style="list-style-type: none"> 1. From before the test begins to the conclusion of a 1 hour post-test observation period, no fire or explosion shall occur.
4.4 Immersion Test			
	Simulates a situation where the vehicle is flooded.	<p>Complete battery system tested IAW SAE J2464, Sect. 4.3.5, with following exceptions:</p> <ol style="list-style-type: none"> 1. Contactors are to be closed at start of test all vehicle interface connections are in place to simulate vehicle in use condition. 2. Contactor control and battery monitoring system are connected and operational. All electronic control modules connected and in operational power state. 3. Battery system fully submerged within 5 min following initial contact with water. 	<ol style="list-style-type: none"> 1. During the test, no rupture, fire, or explosion shall occur.

Tests	Description	Conditions	Required Outcome
4.5 Mechanical Shock			
(Alternative 1: Complete battery system test)	Simulates inertial loads which may occur during a vehicle crash situation, using a battery system-level test.	Complete battery system tested IAW either U.N. Test Manual, Test T.4, or SAE J2464, Sect. 4.3.1, with following exceptions: 1. Evaluations, one repetition each, conducted in positive and negative directions of vehicle longitudinal and lateral axes, as installed, for a total of four evaluation conditions. 2. Battery system firmly secured to the test fixture. Note that while battery modules or sections may be individually tested IAW U.N. requirements, a complete battery system is to be tested for this condition, except as allowed by per 4.1.3 of J2929.	1. From before the test begins to the conclusion of a 1 hour post-test observation period, no enclosure rupture, fire, or explosion shall occur. 2. High voltage to ground isolation of at least 100 Ω/V shall be maintained (measured IAW ISO 6469-1, Sect. 6.1.3 or equivalent).
(Alternative 2: Vehicle-Level Evaluation)	Simulates inertial loads which may occur during a vehicle crash situation, using a vehicle-level test.	Complete battery system assessed following vehicle tests simulating front, rear, and side impacts, as defined in FMVSS 305, S6.1, 6.2, 6.3 with the following clarification: battery state of charge shall be at the maximum possible during normal vehicle operation and battery temperature shall be 25°C +/- 5°C.	1. From before the test begins to the conclusion of a 1 hour post-test observation period, no enclosure rupture, fire, or explosion shall occur. 2. High voltage to ground isolation of at least 100 Ω/V shall be maintained (measured IAW ISO 6469-1, Sect. 6.1.3 or equivalent). 3. The battery system shall be retained at its mounting location.
4.6 Battery Enclosure Integrity			
(Alternative 1: Battery system-level evaluation – application specific)	Simulates contact loads which may occur during a vehicle crash situation, using a battery system-level test.	Complete battery system tested IAW SAE J2464, Sect. 4.3.6, with following exceptions: 1. Crush condition shall simulate expected battery enclosure intrusion for each condition defined in FMVSS 305, S6.1, 6.2, and 6.3. 2. Battery state of charge shall be at the maximum possible during normal vehicle operation and battery temperature shall be 25°C +/- 5°C. 3. Magnitude, direction, location, and loading surface size and shape of crush shall simulate in-vehicle crash condition. 4. If vehicle structure is used as part of all of battery enclosure, that structure shall be included in the test.	1. From before the test begins to the conclusion of a 1 hour post-test observation period, no enclosure rupture, fire, or explosion shall occur. 2. High voltage to ground isolation of at least 100 Ω/V shall be maintained (measured IAW ISO 6469-1, Sect. 6.1.3 or equivalent).

Tests	Description	Conditions	Required Outcome
(Alternative 2: Battery system-level evaluation – generic)	Simulates contact loads which may occur during a vehicle crash situation, using a battery system-level test.	Complete battery system tested IAW SAE J2464, Sect. 4.3.6, with following exceptions: 1. Extent of crush specified in SAE J2464, Sect. 4.3.6.1 is not applicable. 2. Crush shall continue until a force of 100 kN is achieved.	1. From before the test begins to the conclusion of a 1 hour post-test observation period, no enclosure rupture, fire, or explosion shall occur. 2. High voltage to ground isolation of at least 100 Ω/V shall be maintained (measured IAW ISO 6469-1, Sect. 6.1.3 or equivalent).
(Alternative 3: Vehicle-Level Evaluation)	Simulates contact loads which may occur during a vehicle crash situation, using a vehicle-level test.	Complete battery system assessed following vehicle tests simulating front, rear, and side impacts, as defined in FMVSS 305, S6.1, 6.2, 6.3 with the following clarification: battery state of charge shall be at the maximum possible during normal vehicle operation and battery temperature shall be 25°C +/- 5°C.	1. From before the test begins to the conclusion of a 1 hour post-test observation period, no enclosure rupture, fire, or explosion shall occur. 2. High voltage to ground isolation of at least 100 Ω/V shall be maintained (measured IAW ISO 6469-1, Sect. 6.1.3 or equivalent). 3. The battery system shall be retained at its mounting location.
4.7 Exposure to Simulated Vehicle Fire			
	Simulates exposure to vehicle fire condition to verify that the battery system does not pose additional risk due to explosion.	Complete battery system subjected to a high temperature heat and flame environment until the battery system is fully involved in the fire. Then external heat and flame source is removed and battery system allowed to continue burning. Test complete and post-observation period begins when there is no longer visible flame.	1. During the test, and for a 1 hour post-test observation period, no battery system component or any portion of a component shall penetrate a wire mesh screen which surrounds the battery system.
4.8 Electrical Short Circuit			
	Simulates a short circuit condition across the battery terminals.	Complete battery system tested IAW either U.N. Test Manual, Test T.5, or the pack hard short circuit condition defined in SAE J2464, Sect. 4.5.1, with following exceptions/clarifications: 1. Evaluation in SAE J2464, Sect. 4.5.1 which disables protection devices is not to be included. 2. All battery system electronic control modules connected and in operational power state. 3. Spark source or gas concentration measuring device required at minimum of one location, selected to be at highest potential for gas leaks.	1. During the test, no rupture, fire, or explosion shall occur. In the event a gas concentration measuring device is used, flammable gas concentration shall not exceed the lower flammability limit in air.

Tests	Description	Conditions	Required Outcome
4.9 Single Point Overcharge Protection System Failure			
	Simulates condition where battery charge device is no longer being controlled and failure may allow battery system to be overcharged.	<ol style="list-style-type: none"> 1. Charge the battery system at maximum possible rate for the application. Continue charging until charge device voltage is reached or connection interface disconnects battery from charge device. 2. Battery system operated under normal operating conditions with cooling system operating. Integrated, passive circuit protection devices operational. Active charge control disabled/disconnected. 3. Spark source or gas concentration measuring device required at minimum of one location, selected to be at highest potential for gas leaks. 	<ol style="list-style-type: none"> 1. During the test and for a 1 hour post-test observation period, no rupture, fire, or explosion shall occur. In the event a gas concentration measuring device is used, flammable gas concentration shall not exceed the lower flammability limit in air.
4.10 Single Point Over Discharge Protection System Failure			
	Simulates condition where battery system discharge load is no longer being controlled and failure may allow battery system to be over discharged.	<ol style="list-style-type: none"> 1. Discharge the battery system at a 1C rate for HEV/PHEV applications or at a C/3 rate for EV applications Continue discharging until connection interface disconnects or battery voltage reaches 0.0V +/- 0.2V. 2. Battery system operated under normal operating conditions with cooling system operating. Integrated, passive circuit protection devices operational. Active charge control disabled/disconnected. 3. Spark source or gas concentration measuring device required at minimum of one location, selected to be at highest potential for gas leaks. 	<ol style="list-style-type: none"> 1. During the test and for a 1 hour post-test observation period, no rupture, fire, or explosion shall occur. In the event a gas concentration measuring device is used, flammable gas concentration shall not exceed the lower flammability limit in air.

Tests	Description	Conditions	Required Outcome
4.11 Single Point Thermal Control System Failure			
	Simulates condition where battery system temperature control is no longer operating and failure may lead to a battery system over temperature condition.	Complete battery system tested IAW SAE J2464, Sect. 4.4.3, with following exceptions/clarifications: 1. Full charge and discharge cycle means a change in state of charge from the minimum normal operating SOC to the maximum normal operating SOC. 2. Charge rate is maximum normal rate for battery system. 3. Battery system operated under normal operating conditions with cooling system disabled. Integrated, passive circuit protection devices operational. 4. Spark source or gas concentration measuring device required at minimum of one location, selected to be at highest potential for gas leaks.	1. During the test and for a 1 hour post-test observation period, no rupture, fire, or explosion shall occur. In the event a gas concentration measuring device is used, flammable gas concentration shall not exceed the lower flammability limit in air.
4.12 Fault Analysis			
	Verifies through fault analysis that plausible single point faults will not result in fire, explosion, rupture, or high-voltage hazard.	Perform and document fault analysis of battery system according to defined and documented method such as SAE J1739.	1. Complete and documented fault analysis showing that plausible single point faults will not result in fire, explosion, rupture, or high-voltage hazard.
4.13 Protection against High-Voltage Exposure			
(Automatic Disconnects)	Verifies automatic disconnect operation.	Trigger automatic disconnect (conditions which result in actuation are vehicle-application specific).	1. Measured voltage less than 60 VDC at 5 s after actuation.
(Manual Disconnects)	Verifies battery system provides one of two options for protecting against high-voltage exposure in the event of automatic disconnect failure.	Option 1: Exercise manual method for removing voltage between positive and negative output terminals. Option 2: Verify by inspection whether access to high-voltage conductors is finger-proof.	Option 1: Measured voltage less than 60 VDC at 5 s after actuation. Option 2: Access to high-voltage conductors is finger-proof.
(Protection against Direct High-Voltage Contact)	Verifies battery enclosure as installed meets ISO/DIS 6469-3.2, Sect. 7.6.	Verify compliance by inspection.	Cited standard is met.

8.2 Electric and Hybrid Vehicle Rechargeable Energy Storage System Safety and Abuse Testing, SAE J2464 (2009)

Scope: Recommended procedures (not standards) to characterize response of RESS to off-normal conditions or environments that may occur as a result of operator negligence, vehicle accidents, device or system defects, poorly informed or trained users or mechanics, failure of specific RESS control and support hardware, or transportation/handling incidents or accidents (Table 8-4).

Table 8-4. Summary of the tests in SAE J2464.

Tests	Description	Conditions	Data Recorded
4.2 Hazardous Substance Monitoring	Perform quantitative analysis of hazardous substance release under various conditions.		
Test 1: Electrolyte Vapor Analysis	Open container of liquid electrolyte in closed chamber.	1. Sufficient amount of electrolyte to saturate the gas volume at upper operation temperature of cell or 50°C, whichever is higher, and >90% humidity.	1. Sample vapors after 60 min at temperature.
Test 2: Cell Forced Vent without thermal runaway	Cell exposed to the following abusive conditions: a. Thermal stability at elevated temperature b. Overcharge c. Overdischarge	1. Cell exposed to each abusive condition in succession.	1. Sample vapors if venting occurs.
Test 3: Cell Forced Vent with thermal runaway	Cell is forced into thermal runaway (method at discretion of tester).	1. Method chosen to maximize likelihood of venting.	Sample vapors after thermal runaway achieved.
Test 4: Pack-Level Electrolyte Vapor Analysis in conjunction with one other pack-level abuse test where combustion expected	Pack is subjected to another abuse test involving combustion.	1. Total containment of pack not required. 2. Spark source should be present.	Localized sampling of combustion products during a test.
4.3.1 Shock			
	At cell level or above, subject unit to shock events at one or more defined shock levels.	1. Subject cells to test levels from U.N. Manual of Tests and Criteria, Sect. 38.3. 2. Subject packs to 25g shock, 15ms duration (half sine) for 3 repeats on each axis in both positive and negative directions (18 total).	1. Record condition of unit including temp, voltage, resistance, mass, and physical dimensions before and after test.

Tests	Description	Conditions	Data Recorded
4.3.2 Drop Test (Pack)			
	Free fall drop test in most vulnerable orientation.	1. Drop from 2 meters onto a flat, hard surface.	1. Observe for at least 1 hour after test. 2. Record condition of unit including temp, voltage, resistance, mass, and physical dimensions before and after test.
4.3.3 Penetration			
	Penetrate the unit with a conductive steel rod (cell, module, or pack).	1. Subject cells to 3mm sharp rod at 8 cm/s or greater rate, run through cell. 2. Subject modules and packs to 20mm sharp rod at 8 cm/s or greater rate, run through 3 cells or 100mm (whichever is greater). 3. Spark source should be present during test.	1. Observe for at least 1 hour after test. 2. Record condition of unit including temp, voltage, resistance, mass, and physical dimensions before and after test.
4.3.4 Roll-over Test			
	For module or pack. Rotate the unit through a range of orientations.	1. Rotate the unit one complete revolution in 1 min in a continuous slow roll fashion. 2. Rotate unit in 90 deg increments for one full revolution, pausing 1 hour in each orientation.	1. Observe during and for at least 1 hour after test for any material leakage. 2. Record condition of unit including temp, voltage, and resistance before and after test.
4.3.5 Immersion Test			
	For module or pack. Submerge the unit in salt water for at least 2 hours.	1. Water shall be ambient temperature with 5% salt by weight, enough to completely submerge module or pack.	1. Observe for a minimum of 2 hours (submerged) or until visible reactions have ceased. 2. Record condition of unit including temp, voltage, and resistance before, during, and after test. 3. Sample gases to measure potential gases produced by electrolysis of water.

Tests	Description	Conditions	Data Recorded
4.3.6 Crush Test			
	Crush between a fixed surface and a crush fixture that results in sufficient deformation to cause shorting.	<ol style="list-style-type: none"> 1. Crush in at least two of three axes. 2. Force no more than 1000 times weight of unit under test. 3. Crush to 85% initial dimension then hold 5 min. Then continue crush to 50% initial dimension. 4. Spark source should be present during test. 	<ol style="list-style-type: none"> 1. Observe for at least 1 hour after test. 2. Record acceleration force on unit, temperature, voltage, resistance, and mass before and after test.
4.4.1 High-Temperature Hazard Test			
	Subject unit under test (pack module or system) to temperatures representing a fuel fire and evaluate explosion hazard.	<ol style="list-style-type: none"> 1. Heat to nominal 890°C using radiant (non-contact) heating within 90 seconds and hold for 10 minutes. 	<ol style="list-style-type: none"> 1. Record unit, temperature, voltage, and resistance. 2. Sample gases to measure potential gases produced by electrolysis of water.
4.4.2 Thermal Stability Test			
	The unit (cell) is heated incrementally in a chamber while monitoring self temperature to detect any self-heating or thermal runaway.	<ol style="list-style-type: none"> 1. Heat to 300°C above maximum operating temperature while monitoring cell temperature. 2. Increase temperature in 5°C increments and hold for 30 min at each increment. 3. Run test with fully charged cell then repeat with overcharged cell, mid-life cell, and end-of-life cell. 4. Spark source should be present during test. 	<ol style="list-style-type: none"> 1. Record unit and chamber temperatures during test. 2. Record voltage and resistance during test. 3. Flammability of any solids, liquids, or gases released should be analyzed. 4. Record unit mass before and after test.
4.4.3 Cycling without Thermal Management			
	The unit (module or pack) is fully charged and discharged (at a rate comparable to the intended application) with active thermal controls disabled.	<ol style="list-style-type: none"> 1. Start fully charged at nominal operating temperature. 2. Conduct 20 full charge/discharge cycles with no rest period between charge and discharge. 3. Spark source should be present during test. 	<ol style="list-style-type: none"> 1. Record unit temperature during test. 2. Record voltage and resistance during test. 3. Flammability of any solids, liquids, or gases released should be analyzed.

Tests	Description	Conditions	Data Recorded
4.4.4 Thermal Shock Cycling			
	The unit (cell, module, or pack) is fully charged and subjected to fast cycling between temperature extremes.	<ol style="list-style-type: none"> 1. Start fully charged with active thermal controls disabled. 2. Cycle ambient temperature between 70°C and -40°C, with dwell times as follows: Cell: 1 hour Module: 6 hours Pack: time required to reach uniform temperature. 3. Perform five complete cycles, with three C/3 discharge cycles at 25°C ambient before and after test (using manufacturers recharge algorithm). 	<ol style="list-style-type: none"> 1. Record unit temperature during test. 2. Record voltage during test. 3. Record voltage and resistance of case with respect to positive and negative terminals before and after test. 4. Measure unit capacity before and after test. 5. Measure unit mass before and after test.
4.4.5 Passive Propagation Resistance Test			
	The unit (module or pack) is subjected to a single-cell thermal runaway event to evaluate whether this even propagates to adjacent cells.	<ol style="list-style-type: none"> 1. Start fully charged with all external circuits, cooling systems, etc. disabled. 2. Heat the unit until all cells stabilize at 55°C or maximum operating temp (whichever is greater). Heat one cell uniformly to 400°C (or until cell enters thermal runaway) in less than 5 min. Then turn heater off and observe for 1 hour. 3. Repeat with other cells in module/pack that represent various thermal environments/relationships in the pack. 	<ol style="list-style-type: none"> 1. Record unit temperature on all sides during test. 2. Record voltage during test. 3. Record voltage and resistance of case with respect to positive and negative terminals before and after test.
4.5.1 Short Circuit Tests			
	Short circuits applied at various impedances and locations in unit (cell and module or pack)	<ol style="list-style-type: none"> 1. Apply short in less than 1 sec between positive and negative terminals for 1 hour or until another condition occurs that stops the test. 2. All active protection devices shall be disabled. 3. Observe unit for an additional 1 hour period. 4. Spark source should be present during test. 	

Tests	Description	Conditions	Data Recorded
Test 1: Cell Hard Short	Hard short applied between positive and negative terminal of a single cell.	<ol style="list-style-type: none"> 1. Apply hard short across terminals of a single cell. If pack design uses cells in parallel, test shall be performed within a module or with the cell electrically and thermally connected as if it were in a module. For packs with modules in parallel, test shall be performed with all modules connected as expected in the field. 2. All passive protection devices should be disabled or bypassed (optional to repeat test with passive protection devices operational). 	<ol style="list-style-type: none"> 1. Record unit temperature at a minimum of three locations on unit during test. 2. Record current and cell voltage during test. 3. Record voltage and resistance of case with respect to positive and negative terminals before and after test. 4. Record unit mass before and after test. 5. Flammability of any solids, liquids, or gases released should be analyzed.
Test 2: Cell Soft Short	Soft short applied between positive and negative terminal of a single cell.	<ol style="list-style-type: none"> 1. Apply soft short across terminals of a single cell, where the short impedance shall be comparable to the DC impedance of the elements within the unit being shorted. If pack design uses cells in parallel, test shall be performed within a module or with the cell electrically and thermally connected as if it were in a module. For packs with modules in parallel, test shall be performed with all modules connected as expected in the field. 2. All passive protection devices should be disabled or bypassed (optional to repeat test with passive protection devices operational). 	<ol style="list-style-type: none"> 1. Record unit temperature at a minimum of three locations on unit during test. 2. Record current, voltage during test. 3. Record voltage and resistance of case with respect to positive and negative terminals before and after test. 4. Record unit mass before and after test. 5. Flammability of any solids, liquids, or gases released should be analyzed.
Test 3: Module Hard Short	Hard short applied between positive and negative terminal of a single module.	<ol style="list-style-type: none"> 1. Apply hard short across terminals of a single module. For packs with modules in parallel, test shall be performed with all modules connected as expected in the field. 2. All passive protection devices should be disabled or bypassed (optional to repeat test with passive protection devices operational). 	<ol style="list-style-type: none"> 1. Record unit temperature at a minimum of three locations on unit during test. 2. Record current, voltage during test. At pack level, record individual cell voltage during test wherever possible. 3. Record voltage and resistance of case with respect to positive and negative terminals before and after test. 4. Record unit mass before and after test. 5. Flammability of any solids, liquids, or gases released should be analyzed.

Tests	Description	Conditions	Data Recorded
Test 4: Pack Hard Short	Hard short applied between positive and negative terminal of the pack.	<ol style="list-style-type: none"> 1. Apply hard short across terminals of the pack, with the terminals of the pack live prior to the short as in a driving condition. 2. Active protection elements shall not be used. 3. Repeat the test with all passive protection devices should be disabled or bypassed. 	<ol style="list-style-type: none"> 1. Record unit temperature at a minimum of three locations on unit during test. 2. Record current, voltage during test. At pack level, record individual cell voltage during test wherever possible. 3. Record voltage and resistance of case with respect to positive and negative terminals before and after test. 4. Record unit mass before and after test. 5. Flammability of any solids, liquids, or gases released should be analyzed.
4.5.2 Overcharge Test			
	The unit (cell and module or pack) is subjected to overcharging.	<ol style="list-style-type: none"> 1. Cells should be charged at two rates: a) 1 C-rate constant current, and b) High-rate overcharge at maximum current that can be supplied by the regenerative braking or charging system (or 3C if maximum not yet known). Charge until at least 200% SOC is reached or test terminated by other destructive factor such as thermal runaway. 2. Modules and packs should be charged at 1 C-rate constant current until at least 200% SOC is reached or test terminated by other destructive factor such as thermal runaway. 3. Passive integrated overcharge protection shall remain enabled throughout the test, but all active protection devices shall be disabled prior to the test. 4. Spark source should be present during test. 	<ol style="list-style-type: none"> 1. Record unit temperature during test. 2. Record current and voltage during test. 3. Flammability of any solids, liquids, or gases released should be analyzed. 4. Record unit mass before and after test. <p>Additionally for modules and packs:</p> <ol style="list-style-type: none"> 5. Record unit temperature at a minimum of three locations on unit during test. 6. Record individual cell voltages during test wherever possible. 7. Record voltage and resistance of case with respect to positive and negative terminals before and after test.

Tests	Description	Conditions	Data Recorded
4.5.3 Overdischarge (Forced Discharge) Test			
Test 1: Cell Test	The cell is subjected to discharge for two times the cell capacity in amp-hours.	<ol style="list-style-type: none"> 1. Discharge cell at maximum recommended continuous current for duration of two times cell capacity in Ah. Voltage at end of forced discharged shall be maintained for 30 min. 2. Voltage applied to the unit shall not exceed $-V_{max}$ (V_{max} = maximum recommended voltage of cell). 3. Passive integrated overdischarge protection shall remain enabled throughout the test, but all active protection devices shall be disabled prior to the test. 4. Spark source should be present during test. 	<ol style="list-style-type: none"> 1. Record cell temperature during test. 2. Record current and voltage during test. 3. Flammability of any solids, liquids, or gases released should be analyzed. 4. Record cell mass before and after test. 5. Observe cell for 1 hour after test completion.
Test 2: Module Test	The module is subjected to discharge for two times the cell capacity in amp-hours.	<ol style="list-style-type: none"> 1. For multi-cell series configuration in module, a completely discharged cell is to be force-discharged by connecting it in series with fully charged cells of the same kind. 2. Discharge at maximum recommended current until module voltage reaches $0.0 \pm 0.2V$. Voltage shall be maintained for 30 min. 3. Voltage applied to the unit shall not exceed $-V_{max}$ (V_{max} = maximum recommended voltage of cell). 4. Passive integrated overdischarge protection shall remain enabled throughout the test, but all active protection devices shall be disabled prior to the test. 5. Spark source should be present during test. 	<ol style="list-style-type: none"> 1. Record unit temperature at a minimum of three locations on unit during test. 2. Record current and voltage of every cell for multi-cell series configuration at pack level. 3. Record voltage and resistance of case with respect to positive and negative terminals before and after test. 4. Record evidence of cell leakage or rupture. 5. Observe cell for 1 hour after test completion.
4.5.4 Separator Shutdown Integrity Test			
Note: Applies only to cells that have a shutdown separator	The cell is tested at elevated temperatures in a series-connected configuration to evaluate the efficacy of the shutdown separator.	<ol style="list-style-type: none"> 1. Heat cell to at least $5^{\circ}C$ above measured shutdown temperature. Once temperature has stabilized for 10 min. apply the high-level overvoltage (at least 20V) with a current limit of less than 1C. Maintain the applied voltage for at least 30 min. or until the separator fails. 	<ol style="list-style-type: none"> 1. Record cell temperature during test. 2. Record voltage and current during test. 3. Record cell mass before and after test.

8.3 U.N. Transport of Dangerous Goods Manual of Tests and Criteria, 5th Revision, Section 38.3 (2010)

Scope: Section 38.3 presents test procedures for the classification of lithium metal and Li-ion cells and batteries (Table 8-5).

Table 8-5. Summary of the tests in the U.N. Transport Manual.

Tests	Description	Conditions	Required Outcome
Test T.1 Altitude Simulation	Simulate air transport under low-pressure conditions.	1. Test cells and batteries stored at a pressure of 11.6 kPa or less for at least six hours at ambient temperature (20°C +/- 5°C).	1. No mass loss, disassembly, leakage, venting, rupture, or fire. 2. Post-test open circuit voltage not less than 90% of pre-test voltage.
Test T.2 Thermal Test	Assesses cell and battery seal integrity and internal electrical connections using rapid and extreme temperature changes.	1. Test cells and batteries stored for at least six hours at a test temperature equal to 75°C +/- 2°C, followed by storage for at least six hours at a temperature equal to -40°C +/- 2°C. Maximum time interval between temperature extremes is 30 minutes. 2. Repeat temperature cycle 10 times, then store test articles for 24 hours at 20°C +/- 5°C. 3. For large cells and batteries, dwell time at extremes shall be at least twelve hours instead of six.	1. No mass loss, disassembly, leakage, venting, rupture, or fire. 2. Post-test open circuit voltage not less than 90% of pre-test voltage.
Test T.3 Vibration	Simulates vibration during transport.	1. Firmly attached to vibration machine to faithfully transmit the vibration. 2. Waveform shall be sinusoidal with a logarithmic sweep between 7Hz and 200Hz, and back to 7 Hz, traversed in 15 minutes. 7 – 18 Hz at 1g, amplitude then maintained at 0.8mm and frequency increased until 8g is attained (around 50Hz), then 8g is maintained up to 200Hz. 3. Repeat twelve times for a total of 3 hours for each of three mutually perpendicular mounting faces.	1. Sample vapors if/when venting occurs during test.

Tests	Description	Conditions	Required Outcome
rTest T.4 Shock Test	Simulates possible impacts during transport.	<ol style="list-style-type: none"> 1. Secured to the testing machine by means of a rigid mount. 2. Each cell or battery subjected to a half-sine shock of peak acceleration of 150g and pulse duration of 6ms. 3. Each cell or battery shall be subjected to three shocks in the positive direction followed by three shocks in the negative direction of three mutually perpendicular mounting positions for a total of 18 shocks. 4. For large cells and batteries, the shock peak acceleration shall be 50g and pulse duration of 11ms. 	<ol style="list-style-type: none"> 1. No mass loss, disassembly, leakage, venting, rupture, or fire. 2. Post-test open circuit voltage not less than 90% of pre-test voltage.
Test T.5 External Short Circuit	Simulates an external short circuit.	<ol style="list-style-type: none"> 1. Cell or battery shall be temperature stabilized so external case temperature reaches 55°C +/- 2°C. 2. Short circuit applied with total external resistance less than 0.1 ohms, for at least one hour after the cell or battery has returned to the starting temperature. 	<ol style="list-style-type: none"> 1. External temperature does not exceed 170°C. 2. No disassembly, rupture, or fire within six hours of conclusion of test.
Test T.6 Impact	Simulates an impact.	<ol style="list-style-type: none"> 1. Cell placed on flat surface with 15.8 mm diameter bar placed across center of cell. A 9.1 kg mass is dropped from a height of 61 +/- 2.5 cm onto the cell. 2. Subject each sample to a single impact (separate samples for each impact). <p>Note: A cylindrical or prismatic cell should be impacted with its longitudinal axis parallel to the flat surface and perpendicular to the longitudinal axis of the 15.8 mm diameter curved surface lying across the center of the cell. A coin or button cell is to be impacted with the flat surface of the sample parallel to the flat surface and the 15.8 mm curved surface lying across its center.</p>	<ol style="list-style-type: none"> 1. External temperature does not exceed 170°C. 2. No disassembly or fire within six hours of conclusion of test.

Tests	Description	Conditions	Required Outcome
Test T.7 Overcharge	Evaluates ability of a rechargeable battery to withstand an overcharge condition.	<ol style="list-style-type: none"> 1. Charge battery at a charge current twice the manufacturer's recommended maximum recommended charge current. Minimum voltage of the test shall be: <ol style="list-style-type: none"> a) if recommended charge voltage is not more than 18V, minimum test voltage shall be lesser of two times the maximum charge voltage or 22V. b) if recommended charge voltage is more than 18V, minimum test voltage shall be 1.2 times the maximum charge voltage. 2. Conduct test at ambient temperature. 3. Test duration shall be 24 hours. 	<ol style="list-style-type: none"> 1. No disassembly or fire within seven days of test.
Test T.8 Forced Discharge	Evaluates ability of a primary or rechargeable battery to withstand a forced discharge condition.	<ol style="list-style-type: none"> 1. Cell shall be discharged at ambient temperature by connecting it in series with a 12VDC power supply at an initial current equal to the specified maximum discharge current. 2. Specific discharge current is to be obtained by connecting a resistive load of the appropriate size and rating in series with the test cell. 3. Cell shall be forced discharged for a time interval (in hours) equal to its rated capacity divided by the initial test current (in amperes). 	<ol style="list-style-type: none"> 1. No disassembly or fire within seven days of test.

8.4 Safety Tests for Li-ion Batteries in UL1642 (2005)

Table 8-6. Summary of the tests in UL 1642.

Test	Description	Number of Cells	Required Outcome
Electrical Tests			
Short circuit (23°C)	<0.1 Ω to 0.1 V, monitor until T returns to 33°C.	5 fresh charged, 5 cycled charged	No explosion, no fire, $T_{\text{cell}} < 150^{\circ}\text{C}$
Short circuit (55°C)	<0.1 Ω to 0.1 V, monitor until T returns to 65°C.	5 fresh charged, 5 cycled charged	No explosion, no fire, $T_{\text{cell}} < 150^{\circ}\text{C}$
Abnormal charge	Charge at 3 times manufacturers' recommended rate for 7h.	5 fresh charged, 5 cycled charged	No explosion, no fire
Forced discharge	One discharged cell in series with the number of series-connected cells (charged) used in the device. Discharge the series assembly through a resistance <0.1 Ω to 0.1 V. Monitor until T returns to 10°C above ambient.	5 fresh charged, 5 cycled charged	No explosion, no fire
Mechanical tests			
Flat plate crush	Between flat surfaces to 18 kN.	5 fresh charged, 5 cycled charged	No explosion, no fire
Impact test	15.8 mm diameter bar placed across cell or battery. 9.1 kg weight dropped onto the bar from a height of 61 cm. Prismatic cells to be testing in both directions. 3 axis, minimum 75 g, peak 125 to 175 g.	5 fresh charged, 5 cycled charged	No explosion, no fire
Shock test	3 axis, minimum 75 g, peak 125 to 175 g.	5 fresh charged, 5 cycled charged	No explosion, no fire, no leaking, no venting
Vibration test	0.8 mm amplitude, 10 to 55 Hz at a rate of 1 Hz.min and back again.	5 fresh charged, 5 cycled charged	No explosion, no fire, no leaking, no venting
Environmental tests			
Heating test	Heat to 130°C at 5/min, and hold at 130°C for 10 min. Return to room temperature and examine.	5 fresh charged, 5 cycled charged	No explosion, no fire
Temperature cycling test	Room T: 4 h, 70°C: 4 h, room T: 4h, -40°C: 4 h, room T: 4 h: repeat cycle 10 times.	5 fresh charged, 5 cycled charged	No explosion, no fire, no leaking, no venting
Altitude test	11.6 kPa for 6 hr	5 fresh charged, 5 cycled charged	No explosion, no fire, no leaking, no venting
Projectile test	Cells are incinerated.	5 fresh charged	Cell parts cannot penetrate the wire screen used in the test

Note: The projectile test is one in which the cells are heated on a screen over a burner. When they explode or vent and burn, the cells must not puncture the screen on which they rest by projectiles produced by the event.

8.5 Batteries for Use in Electric Vehicles, UL 2580 (2011)

Scope: Electrical energy storage assemblies such as battery packs and the subassembly/modules that make up these assemblies for use in electric-powered vehicles (Table 8-7). This standard evaluates the electrical energy storage assembly's ability to safely withstand simulated abuse conditions and prevents any exposure of persons to hazards as a result of the abuse. This standard evaluates the electric energy storage assembly and modules based upon the manufacturer's specified charge and discharge parameters at specified temperatures

Table 8-7. Summary of the battery and subsystem level tests in UL 2580.

Tests	Description	Conditions	Required Outcome
13 Overcharge Test			
	<p>Evaluate EESA and its associated protection circuitry ability to withstand an overcharge condition.</p> <p>Testing may be conducted on a subassembly instead if determined to be representative of the EESA.</p>	<ul style="list-style-type: none"> Fully discharged sample Subjected to the maximum specified charging rate of the battery assembly (single fault condition in the charging circuit of the pack). Test continues until ultimate results occur. Spark ignition source used to detect the presence of flammable concentrations of gases. 	<ol style="list-style-type: none"> No evidence of fire or explosion Minimum isolation resistance of $100\ \Omega/V$ No venting of vapors No rupture of EESA or evidence of electrolyte leakage If operational after test it will operate as intended through a discharge and charging cycle.
14 Short Circuit Test			
	<p>Determine ability of an EESA ability to withstand an external short circuit.</p> <p>Testing may be conducted on a subassembly instead if determined to be representative of the EESA.</p>	<ol style="list-style-type: none"> Fully charged samples Sample to be short-circuited by a circuit load having a total resistance \leq to $20\ m\ \Omega$. Spark ignition source used to detect the presence of flammable concentrations of gases. 	<ol style="list-style-type: none"> No evidence of fire or explosion Minimum isolation resistance of $100\ \Omega/V$ No venting of vapors No rupture of EESA or evidence of electrolyte leakage If operational after test it will operate as intended through a discharge and charging cycle.

Tests	Description	Conditions	Required Outcome
15 Overdischarge Protection Test			
	<p>Determine ability to withstand an overdischarge condition.</p> <p>Testing may be conducted on a subassembly instead if determined to be representative of the EESA.</p>	<ul style="list-style-type: none"> Conducted with all discharge protection circuitry for both temperature and minimum voltage connected to prevent irreparable cell damage. Fully charged samples Subjected to a constant discharging current that will discharge a battery at 95% of the passive protection device ratings. Test continues until the passive protection devices are activated, or the minimum cell voltage/maximum temperature protection is activated. Spark ignition source used to detect the presence of flammable concentrations of gases. 	<ol style="list-style-type: none"> No evidence of fire or explosion Minimum isolation resistance of 100 Ω /V No venting of vapors No rupture of EESA or evidence of electrolyte leakage If operational after test it will operate as intended through a discharge and charging cycle.
16 Temperature Test			
	<p>Determine if modules and their cells are being maintained within their specified operating limits during maximum charge and discharge conditions of the pack.</p> <p>Determine if temperature sensitive safety critical components are maintained within their temperature ratings based upon the maximum operating temperature limits of the pack.</p>	<ul style="list-style-type: none"> Fully discharged EESA Conditioned within a chamber set to the upper limit charging temperature specifications Subjected to maximum normal charging until it reaching specified fully charged condition. Discharged down to specified end of discharge condition Repeated for a total of 10 complete charge and discharge cycles 	<ol style="list-style-type: none"> Specified limits of voltage, current and temperatures measured shall not be exceeded Temperatures measured on components shall not exceed their specifications.
17 Imbalanced Charging Test			
	<p>Determine if an EESA with series connected modules can maintain the cells/modules within their specified operating parameters if it becomes imbalanced.</p>	<ul style="list-style-type: none"> Fully charged sample shall have all of its modules with the exception of one discharged to its specified fully discharged condition. Undischarged module shall be discharged to approximately 50% of its specified state of charge (SOC) to create an imbalanced condition prior to charging. The sample then charged according with manufacturer's specifications. Spark ignition source used to detect the presence of flammable concentrations of gases. 	<ol style="list-style-type: none"> The maximum voltage limit of the module shall not be exceeded when charging an imbalanced EESA. No evidence of fire or explosion Minimum isolation resistance of 100 Ω /V No venting of vapors No rupture of EESA or evidence of electrolyte leakage If operational after test it will operate as intended through a discharge and charging cycle.

Tests	Description	Conditions	Required Outcome
18 Dielectric Voltage Withstand Test			
	<p>Evaluation of the electrical spacings and insulation at hazardous voltage circuits of EESA.</p> <p>Circuits at 60 Vdc or higher subjected to a dielectric withstand voltage consisting of a dc potential of 1.414 times twice rated voltage.</p> <p>An ac potential of 60 Hz at twice rated voltage may be applied instead of the dc potential.</p> <p>Semiconductors or similar electronic components liable to be damaged by application of the test voltage may be bypassed or disconnected.</p>	<ul style="list-style-type: none"> • Test voltage is applied between the hazardous voltage circuits of the sample and non-current carrying conductive parts that may be accessible or connected to accessible parts of a vehicle. • Test voltage is applied between the hazardous voltage charging circuit and charging connections and the enclosure/accessible non-current carrying conductive parts. • If accessible parts are covered with insulating material that may become live in the event of an insulation fault, then the test voltages are applied between each of the live parts and metal foil in contact with the accessible parts. • Test voltages shall be applied for a minimum of 1 min • Cells shall be disconnected from the circuits under test. 	<p>1. No evidence of a dielectric breakdown (breakdown of insulation resulting in a short through insulation/arcing over electrical spacings) as evidenced by an appropriate signal from the dielectric withstand test equipment as a result of the applied test voltage.</p>

Tests	Description	Conditions	Required Outcome
19 Isolation Resistance Test			
	Determine that insulation provides adequate isolation of hazardous voltage circuits from accessible conductive parts of the EESA and that it is non-hygroscopic.	<ul style="list-style-type: none"> DUT (device under test) subjected to isolation resistance test of ISO 6469-1, with the following exceptions: Testing is to be conducted as-received (i.e. no humidity conditioning prior to measurements); and Testing is to be conducted after conditioning in accordance with the Standard for Environmental Testing – Part 2-30: Tests – Test Db: Damp Heat, Cyclic (12 h + 12 h Cycle), IEC 60068-2-30 using the following parameters: <ul style="list-style-type: none"> Variant 1; At maximum temperature of $55 \pm 2^{\circ}\text{C}$ ($131 \pm 3^{\circ}\text{F}$); and 6 cycles. The DUT is to be in the fully charged state For conditioned DUT, upon completion of the 6th cycle of the conditioned DUT, the sample shall be subjected to a controlled recovery in accordance with Recovery, Clause 9, of the Standard for Environmental Testing – Part 2-30: Tests – Test Db: Damp Heat, Cyclic (12 h + 12 h Cycle), IEC 60068-2-30. The isolation resistance measurements shall be made within 30 min of completion of the controlled recovery phase. 	<ol style="list-style-type: none"> The isolation resistance divided by the maximum working voltage of the circuit under test, shall be at least $100 \Omega/\text{V}$.
20 Continuity Test			
	Evaluates the continuity of the protective grounding system of the EESA.	<ul style="list-style-type: none"> Voltage drop in a protective grounding system is measured after applying a test current of 150% of the maximum current of the circuit under test or 25 A, whichever is greater, for 5 s. The supply is to have a no load voltage not exceeding 60 Vdc. Voltage drop measurement is made between any two exposed conductive parts of the assembly. Resistance is calculated from the measured voltage drop and current. 	<ol style="list-style-type: none"> Grounding system of an electric energy storage assembly shall have no more than $0.1\text{-}\Omega$ resistance between any two parts of the system.

Tests	Description	Conditions	Required Outcome
21 Failure of Cooling/Thermal Stability System Test			
	Evaluate the electrical energy storage assembly's ability to safely withstand a failure in the cooling/thermal stability system.	<ul style="list-style-type: none"> DUT (device under test) is fully discharged and then conditioned at maximum specified operating ambient for a period of 7 h. While the DUT, cooling/thermal stability system is disabled, the DUT is charged at its maximum specified charge rate until completely charged or until operation of a protective device. DUT is fully charged and conditioned at maximum specified operating ambient for a period of 7 h. While the DUT cooling/thermal stability system is disabled, the DUT is discharged at the maximum discharge rate until it reaches its specified end of discharge condition or until operation of a protective device. Spark ignition source used to detect the presence of flammable concentrations of gases. Test method is repeated with the DUT conditioned at the minimum specified operating ambient temperature 	<ol style="list-style-type: none"> No evidence of fire or explosion Minimum isolation resistance of 100 Ω /V No venting of vapors No rupture of EESA or evidence of electrolyte leakage If operational after test it will operate as intended through a discharge and charging cycle.
22 Rotation Test			
	<p>A sample of an EESA is subjected to a 360° rotation to simulate an overturned vehicle.</p> <p>Electric energy storage assemblies subjected to a rollover test in accordance with the FMVSS 49 CFR 571 305, need not be subjected to this test.</p> <p>Sample may be mounted within a mounting fixture representative of the intended end use vehicle application.</p>	<ul style="list-style-type: none"> The sample charged to maximum operating state of charge is rotated at a continuous rate of 90°/15 s. Sample is subjected to a 360° rotation in 3 mutually perpendicular different directions. (DUTs with only 2 axes of symmetry, are subjected to 2 mutually perpendicular directions of rotation.) 	<ol style="list-style-type: none"> No evidence of fire or explosion No toxic gas release Minimum isolation resistance of 100 Ω /V If operational after test it will operate as intended through a discharge and charging cycle.

Tests	Description	Conditions	Required Outcome
23 Vibration Endurance Test			
	Evaluate the EESA ability to withstand vibration over the life of the device	<ul style="list-style-type: none"> Vibration endurance test for anticipated end application vehicle vibration profile, or Vibration method outlined in SAE J2380, Vibration Testing of Electric Vehicle Batteries Test pack or module level If module level, use SAE J2380 vibration profile Sample fully charged Sample examined 8 to 24 hr after testing Spark ignition source used to detect the presence of flammable concentrations of gases. 	<ol style="list-style-type: none"> No evidence of fire or explosion Minimum isolation resistance of 100 ohm/V No venting of vapors No rupture of EESA or evidence of electrolyte leakage If operational after test it will operate as intended through a discharge and charging cycle.
24 Shock Test			
	Determine if EESA can withstand a mechanical shock that may occur when in use in an electric vehicle.	<ul style="list-style-type: none"> Sample is fully charged Subjected to SAE J 2464 Shock Test with specified parameters The samples are examined 8 h after the shocks Spark ignition source used to detect the presence of flammable concentrations of gases. 	<ol style="list-style-type: none"> No evidence of fire or explosion Minimum isolation resistance of 100 ohm/V No venting of vapors No rupture of EESA or evidence of electrolyte leakage If operational after test it will operate as intended through a discharge and charging cycle.
25 Drop Test			
	Evaluate whether a hazard exists when a EESA is subjected to an inadvertent drop during installation or removal from the vehicle.	<ul style="list-style-type: none"> Sample is fully charged DUT is dropped from a minimum height of 1.0 m (3.3 ft) to strike a concrete surface in the position most likely to produce the adverse results and in a manner and height most representative of what would occur during maintenance and handling/removal of the EESA during servicing. Samples are examined within a time frame of 6 – 24 h after dropping Spark ignition source used to detect the presence of flammable concentrations of gases. 	<ol style="list-style-type: none"> No evidence of fire or explosion Minimum isolation resistance of 100 ohm/V No toxic gas release If operational after test it will operate as intended through a discharge and charging cycle.

Tests	Description	Conditions	Required Outcome
26 Crush Test			
	Determine EEAS ability to withstand a crush that could occur during a vehicle accident.	<ul style="list-style-type: none"> Sample is fully charged Sample is crushed between a fixed surface and a ribbed test platen in accordance with SAE J2464 EEASs with 3 axes of symmetry, are subjected to 3 mutually perpendicular directions of press. EEASs with only 2 axes of symmetry are subjected to 2 mutually perpendicular directions of press. The maximum force applied to the DUT is to be 100 ± 6 kN Spark ignition source used to detect the presence of flammable concentrations of gases. 	<ol style="list-style-type: none"> Samples shall not explode or catch fire. No toxic gas release
27 Thermal Cycling			
	Assess EESA ability to withstand exposure to rapidly changing environments such as when the vehicle is entering or exiting a heated garage after being in a cold environment, or during transport etc. without evidence of damage that could lead to a hazardous event.	<ul style="list-style-type: none"> Sample is fully charged Subjected to the J2464 thermal shock test except that temperature extremes are from $85 \pm 2^{\circ}\text{C}$ to $-40 \pm 2^{\circ}\text{C}$ ($185 \pm 3^{\circ}\text{F}$ to $-40 \pm 3^{\circ}\text{F}$). 	<ol style="list-style-type: none"> No evidence of fire or explosion Minimum isolation resistance of 100 ohm/V No venting of vapors No rupture of EESA or evidence of electrolyte leakage If still operational sample will operate as intended through two discharge and charging cycles.
28 Salt Spray Test			
	EESA ability to safely withstand anticipated exposure to a salt mist conditions due to either to vehicle use near marine environments, or due to salt de-icing used on roads during winter months.	<ul style="list-style-type: none"> Sample is fully charged Subjected to the test method from the Standard for Environmental Testing - Part 2: Tests - Test Kb: Salt Mist, Cyclic (Sodium Chloride Solution), IEC 60068-2-52, with a severity level of 6. 	<ol style="list-style-type: none"> No evidence of fire or explosion Minimum isolation resistance of 100 ohm/V No venting of vapors No rupture of EESA or evidence of electrolyte leakage If operational after test it will operate as intended through a discharge and charging cycle.
29 Immersion Test			
	Test for those EESA intended for potential immersion (i.e. underbody location). Other applications are evaluated based upon their environmental protection rating.	<ul style="list-style-type: none"> Sample is fully charged Subjected to SAE J2464 Immersion test DUT in its normal operating orientation and with switches/contactors in closed position 	<ol style="list-style-type: none"> No fire or explosion. Minimum isolation resistance of 100 Ω/V

Tests	Description	Conditions	Required Outcome
30 External Fire Exposure Test			
	EESA ability to prevent an explosion as a result of exposure to a simulated fuel or vehicle fire external to the EESA.	<ul style="list-style-type: none"> Fully charged EESA Subjected to a uniform fire source along the length of the assembly at its bottom surface Surface temperatures on the DUT enclosure is monitored Test is concluded when this minimum temperature indication of 590°C (1094°F) has been maintained on the surface for 20 min. Assembly is covered with an aluminum mesh octagonal test cage with mesh flat cover located a maximum of 25.4 mm (1 ft) from the exterior of the DUT sides and top surfaces 	<ul style="list-style-type: none"> No explosion of the DUT that results in projectiles penetrating the mesh test cage
31 Internal Fire Exposure Test			
	EESA shall be designed to prevent a single cell failure within the assembly from cascading into a fire and explosion of the assembly.	<ul style="list-style-type: none"> Sample is fully charged Subjected to the Passive Propagation test of SAE J2464 	1. No fire or explosion of the DUT

8.6 Criteria That Must Be Met to Obtain IEEE 1725 (2011) Certification

Table 8-8. Summary of the tests in IEEE 1725.

Topic	Sub-topic	Sub-sub-topic	Comments
Design requirements			
	Separator selection		
		Stability	Separator needs sufficient chemical, electrochemical, mechanical, and thermal stability.
		Shutdown performance	Separator must have at least two orders of magnitude resistance increase during shutdown at a minimum rate of $2000 \Omega \text{ cm}^2/\text{s}$.
		Strength and thickness	Must provide sufficient strength and thickness to prevent puncture.
		Shrinkage allowance	Separator must extend beyond the negative and positive electrodes in all cases (<i>to prevent electrode contact</i>).
	Electrode design		
		Capacity balance	Reversible charge capacity of negative electrode must be greater than positive electrode (<i>to prevent Li plating</i>).
		Electrode geometry	The active area of the negative electrode must completely cover that of the positive electrode (<i>to prevent Li plating</i>).
	Electrode tables		Optimal tab length required
		Tab insulation	Tab with opposite polarity of case must be insulated (<i>to prevent shorts during shock and vibration</i>).
		Insulation adherence	Insulation needs to be permanently adhered.
		Insulation characteristics	Insulation needs sufficient chemical, electrochemical, mechanical, and thermal stability (<i>for long-term stability</i>).
	Cell vent mechanism		Cell must incorporate a reliable pressure-vent mechanism to avoid dangerous pressure buildup. Pouch cells do not require a vent.
		Retention of contents	Vent mechanism must retain cell contents during venting.
		Projectiles	Cell must pass projectile test of UL1642.
	Overcurrent protection		Cell may incorporate an overcurrent device such as a positive temperature coefficient resistor to limit current in case of short circuit.
	Overvoltage protection		Manufacturer must provide recommended charging current for the cell and upper-voltage limit to the purchaser.

Topic	Sub-topic	Sub-sub-topic	Comments
Manufacturing considerations			
	Materials specifications		Materials specifications must be developed to limit impurities below critical limits.
	Impurity avoidance		All known likely impurities in materials should be identified and controlled.
	Cleanliness		Temperature range, humidity, and dust levels must meet specifications. Metal contamination from equipment or process shall be prevented (<i>to prevent subsequent internal shorts</i>).
	Traceability		All cells must be marked in a way to ensure traceability even during an exothermic event (<i>to find out what went wrong</i>).
	Electrode production		
		Uniform coating	Coating density, thickness, and surface roughness of the electrodes must meet specifications (<i>to ensure cell balance and prevent internal shorts</i>).
		Burr control	Burrs cannot exceed 50% of separator thickness. Burrs on electrodes must be measured once per day at minimum (<i>to prevent internal shorts</i>).
	Prevent damage to electrodes		Wrinkling, tearing, and deformation of electrodes should be prevented. Manufacturer must have a way to detect this.
	Manufacturing equipment		Must prevent damage or modification to the cell.
	Defective electrodes		Must be scrapped.
	Preventive maintenance plan		Must have an effective preventive maintenance plan (i.e., replacement of electrode slitter knives).
	Cell teardown		Cell teardown to ensure specifications are met must be done at least once per machine shift.
Winding or stacking process			
	Care during winding or stacking		
		Tension and damage	Avoid excessive tension or damage by twisting or bending of electrodes.
		Loose material	Must have an effective method to collect all loose material produced in various manufacturing steps (<i>to prevent internal shorts</i>).
		Damaged cells	Must have methods to detect damaged cell cores. Voltage test, resistance test, x-ray check (<i>to prevent internal shorts</i>).
	Electrode spacing		Winding spindle removal process cannot damage the jelly-roll.
	Winding pressure		Pressure selected to avoid cell damage and avoid introduction of burrs, etc.
	No contaminants		No dust, flakes, etc., can be introduced (<i>to prevent internal shorts</i>).

Topic	Sub-topic	Sub-sub-topic	Comments
Assembly precautions			
	No internal shorts		Assembly method and location of insulating material shall provide reliable protection against internal shorts over the lifetime of the cell.
	Tab positioning		
		Staggered	Positive and negative tabs should be staggered so they do not overlap with each other.
		Integrity of cell core	Resistance check to be used to ensure core is undamaged after assembly.
	Insulators		Insulators must be in the proper positions.
	Electrode alignment		Electrode alignment is critical to prevent hazards. Positive electrode must be fully overlapped by negative electrode. 100% of cells must be checked by a vision system to ensure alignment.
Cell ageing			Aging tests must be carried out.
Cell safety			Tests according to UL1642 or IEC 62133 must be carried out and cells must pass all tests.

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9 Codes and Standards Comparison and Gap Assessment

In general, NHTSA approaches safety from a systems engineering perspective, which addresses the safety of components and subsystems through industry standards. NHTSA conducts vehicle-level tests to confirm the safety of the complete vehicle and all subsystems. The objective of this chapter is to identify gaps in safety considerations by codes and standards that NHTSA may want to consider in its review of Li-ion battery vehicle safety. The potential gaps identified are not intended as recommendations for NHTSA regulations. Rather they are assessments of safety issues that both government and industry may choose to consider in developing comprehensive codes and standards.

Industry codes and standards are important for NHTSA in that they complement the FMVSS and define industry consensus on minimum design and test requirements to achieve a desired level of safety, particularly for components and subsystems. Performance-based industry standards support the continued development and evolution of technology, and avoid constraining design and innovation. Performance-based codes and standards help avoid the deployment of incompletely validated and tested designs that might harm safety and help ensure a level playing field for all developers and manufacturers.

The assessment conducted here suggests that codes and standards for Li-ion battery vehicle systems are in their early development stages and immature at this time. As discussed in more detail below, current industry standards do not consider the full duty cycle durability requirements for safety that can be found in industry standards for other vehicle fuel and high-energy storage systems. As a consequence, current Li-ion battery vehicle standards do not support a line item level review of design, manufacturing, and test measures to prevent or mitigate potential failure modes that may be identified in a failure modes and effects analysis or fault tree analysis.

An high-level approach was taken in this codes and standards gap analysis, in which Li-ion battery standards were compared to standards for hydrogen vehicle fuel systems (SAE J2579) as a benchmark of a more mature set of standards. Li-ion battery vehicle technology is following an evolution of technology similar to that for alternative fueled vehicles from the late 1980s forward. While continuing to evolve, hydrogen vehicle fuel systems standards are maturing and provide a rational basis for comparison to practices and standards for other high-energy onboard vehicle systems. It represents automotive industry consensus on minimum design and test requirements to achieve a desired level of safety.

The potential gaps identified here do not suggest that Li-ion battery technology or vehicles are unsafe, but that the technology is still evolving such that an industry consensus on system design and performance-based test methodologies has not been achieved. In this stage of technology development, designs are evolving and highly proprietary, limiting the ability of industry to publicly discuss their knowledge and insights. Individual manufacturers are expected to be conducting their own safety due diligence testing and analysis, while the industry is working to develop a consensus. This is typical of this stage of new technology developments.

There are many parallels drawn in this report between hydrogen storage systems and battery electric storage systems, including the concept of overstress robustness. The purpose is to discuss the need for life cycle durability duty cycle testing of cumulative exposures to abuse followed by worst-case service cycles, among other concepts. This report specifically refers to SAE hydrogen

fuel system standards, rather than standards from other industries, to show that the vehicle industry has previously demonstrated the need for life cycle durability safety requirements. Mechanical stress and durability differ greatly from electro-chemical behavior and durability. Battery cells are a multi-physics combination of electro-chemistry, electrical, mechanical, and thermal processes that do not scale equally with any single parameter such as stress.

The topics and gaps discussed in this chapter include the following.

- High-Level Risk Assessment Context
- Potential Gaps in Component and System Safety Standards
- Potential Gaps in Performance-Based Design Qualification Requirements
 - Potential Gaps in Consideration of Damage, Damage Growth, and Damage Tolerance
 - Potential Gaps in Life Cycle Durability Test Requirements for Each System Level
 - Potential Gaps in Misuse and Abuse Considerations for Durability
- Potential Gaps in Safety Systems Integration and Testing
- Potential Gaps in Systematic Crashworthiness Requirements for Each System Level
- Potential Gaps in Quality Control Requirements.

The observations made here are based upon review of published standards available at the time this work was being conducted and does not consider developments that may be in progress.

9.1 High-Level Risk Assessment Context

This report discusses the potential hazards of Li-ion battery systems for electric and hybrid vehicles. It suggests that the technology and industry has not matured sufficiently to have established comprehensive safety codes and standards that mitigate risks. While codes and standards are not required for any product to operate safely, they represent an industry consensus and collective wisdom to ensure safety.

SAE J1739, Failure Modes and Effects Analysis in Design and in Manufacturing and Assembly Processes, provides a context for basic understanding of the risks under consideration. SAE identifies two “tools” for categorizing and prioritizing risk, the Risk Priority Number (RPN) and the Risk Criticality Number (SO). Risk Criticality is the product of severity (S) and Occurrence (O) rankings ($SO=S*O$). This is the traditional risk ranking based upon severity and likelihood. Risk Priority is the product of the severity, occurrence, and detection (D) rankings ($RPN=S*O*D$). Here S, O, and D are typically defined on a scale of 1 to 10. This categorization includes detectability of failure or errors, recognizing that some high likelihood and severity failures may be fully mitigated through design and process controls. The tables and discussion below from J1739 provide context and insights concerning the need for research and development.

Table 9-1 summarizes the SAE J1739 severity evaluation scale. The most severe failures in this scale, ranks 9 and 10 are failure modes that affect safe vehicle operation and/or involve noncompliance with government regulation. The highest ranking is 10 where the failure mode occurs *without warning*, while 9 addresses those failure modes which occur *with warning*. Severity ranking 7 and 8 address loss of primary function, without affecting safety. Severity rankings 5 and 6 address convenience functions while lower rankings address annoyances and negligible effects.

This investigation is focused on failures that have the potential to affect safe vehicle operation and/or cause harm to passengers, maintenance personnel or first responders. Consequently, all of the failures under consideration have the potential to be categorized as severity levels 9 or 10.

Table 9-1. Summary of SAE J1739 Suggested Severity Evaluation Criteria (emphasis added).

Rank	Category	Criteria: Severity of Effect
10	Safety and/or Regulatory Compliance	Potential failure mode affects safe vehicle operation and/or involves noncompliance with government regulation <i>without</i> warning
9		Potential failure mode affects safe vehicle operation and/or involves noncompliance with government regulation <i>with</i> warning
8	Primary Function Essential	Loss of primary function (vehicle inoperable, does not affect safe vehicle operation)
7		Degradation of primary function (vehicle operable, but at reduced level of performance)
5-6	Secondary Function Convenient	Convenience functions inoperable or at reduced level of performance
2-4	Annoyance	Nonconformance noticed by customers
1	No effect	No discernible effect

Table 9-2 summarizes the SAE J1739 occurrence evaluation scale, i.e. the likelihood of occurrence. It is useful to observe that the distinguishing characteristics for occurrence are

- New technology,
- New design,
- No history, and
- Change in duty cycle and/or operating conditions.

Li-ion technology clearly meets the first criterion for new technology. While vehicle duty cycles are expected to be similar for electric and hybrid vehicles to previous designs, the duty cycle for vehicle batteries and cells is expected to be quite different from duty cycles for other applications such as consumer electronics. This evaluation criteria suggests the likelihood of failure is at least high to very high. SAE J1739 suggests that the likelihood of failure in this range may be 10 to more than 100 per thousand pieces.

Table 9-2. Summary of SAE J1739 Suggested Occurrence Evaluation Criteria.

Rank	Likelihood of Failure	Criteria: Occurrence of Cause
10	Very High	New technology/new design with no history
9	High	Failure is inevitable with new design, new application or change in duty cycle/operating conditions
8		Failure is likely with new design, new application, or change in duty cycle/operating conditions
7		Failure is uncertain with new design, new application, or change in duty cycle/operating conditions
4-6	Moderate	Frequent, occasional or isolated failures associated with similar design or in design simulation and testing
2-3	Low	No or isolated failures associated with similar design or in design simulation and testing
1	Very Low	Failure is eliminated through preventative control

These two tables suggest that the Risk Criticality for Li-ion battery systems may be very high because they are new technology, with potential to affect safe operation of a car. These tables provide no further guidance, other than to gain experience through deployment. However, the RPN addresses the important criterion of detectability of the failure or the error causing failure. As suggested by Table 9-1 above, warnings prior to a safety related failure provide an opportunity to mitigate effects and consequences of the failure. In order to warn, a failure must be detected with sufficient prior notice to take action. Table 9-3 summarizes the suggested ranking for detectability by design control or by process control. This table brings together many of the important elements for improving safety of Li-ion battery systems, including research and development to improve design, testing and damage and failure detection.

Table 9-3. Summary of J1739 Suggested Design and Process Detection Evaluation Criteria.

Rank	Category	Likelihood of Detection by Design Control	Likelihood of Detection by Process Control
10	Absolute Uncertainty	No current design control: cannot detect or is not analyzed	No current process control; cannot detect or is not analyzed
9	Difficult to Detect	Design analysis/Detection controls have a weak detection capability; analysis is not correlated to expected operating conditions	Defect (failure mode) and/or Error (cause) is not easily detected
6-8	Post Design Freeze, Prior to Launch	Product detection through pass/fail testing, test to failure, or degradation	Defect detection by operator (e.g. driver or maintenance personnel), manually or through gauging or controls
3-5	Prior to Design Freeze	Product validation through pass/fail testing, test to failure, or degradation	Defect detection by automated controls and alerts
2	Virtual Analysis – Correlated	Design analysis/detection controls have a strong detection capability	Error (cause) detection by automated controls
1	Detection not applicable: Failure or Error Prevention	Failure cause or failure mode is prevented through design solutions	Error (cause) is prevented

9.2 Potential Gaps in Component and System Safety Standards

As a basic assessment of the status of Li-ion industry codes and standards development, the table of contents for SAE J2464 and J2929 were compared to the table of contents for SAE J2579 for Hydrogen Vehicle Fuel Systems (Table 9-4 and Table 9-5). As a maturing, performance-based standard for onboard vehicle high-energy storage system, SAE J2579 is considered a reasonable benchmark for illustration and discussion purposes. Table 9-1 and Table 9-2 summarize the contents of SAE J2464 and SAE J2929 respectively. Table 9-6 summarizes the contents of SAE J2579, with key terms modified to illustrate a possible outline for Li-ion battery standards. For illustration purposes, “pressure” has been replaced with “voltage,” and “fueling” and “defueling” are replaced with “charging” and “discharging.” While mechanical pressure loadings are clearly very different from electrical voltage, charging, and discharging, an argument can be made for illustration purposes that voltage, charging, and discharging cause damage and degrade safety of battery systems while pressure, fueling, and defueling cause damage and degrade safety of hydrogen fuel systems.

Table 9-7 summarizes the major topic areas considered by SAE J2579 that are not considered in SAE J2464 or J2929. This comparison suggests that there may be gaps in current Li-ion battery standards concerning

- Design,
- Design qualification,
- Production, and
- Vehicle integration.

While we would not expect the standards to have identical outlines, these four topics are major considerations for vehicles, suggesting that there may be fundamental gaps in Li-ion battery standards, when compared to other vehicle energy storage systems standards. Again, this does not imply that the vehicles are unsafe, but that the standards and industry consensus are not yet fully mature. The remainder of this chapter provides more specific insights into key potential gaps in codes and standards.

Table 9-4. Outline of SAE J2464 electric and hybrid electric vehicle RESS safety and abuse testing.

1. SCOPE 1.1 Purpose 2. REFERENCES 2.1 Applicable Publications 2.2 Related Publications 3. DEFINITIONS 4. TECHNICAL REQUIREMENTS 4.1 General Test Guidelines 4.1.1 Number, Condition, and Size of Batteries to be Tested 4.1.2 Types of Abuse Tests Addressed in this Document 4.1.3 Test Conditions and Measurement Accuracies 4.1.4 Hazardous Substance Monitoring 4.1.5 Flammability Determination 4.1.6 Identification of Severity 4.1.7 Measured Data 4.1.8 Test Plans and Reporting 4.2 Hazardous Substance Monitoring Tests (Cell Level and Above) 4.2.1 Test Description 4.2.2 Measured Data	4.3 Mechanical Abuse Tests 4.3.1 Shock Tests (Cell Level or Above) 4.3.2 Drop Test (Pack Level Only) 4.3.3 Penetration Test (Cell Level or Above) 4.3.4 Roll-over Test (Module and Pack Level) 4.3.5 Immersion Test (Module or Pack Level) 4.3.6 Crush Test (Cell Level or Above) 4.4 Thermal Abuse Tests 4.4.1 High Temperature Hazard Test (Pack Module Level and Above) 4.4.2 Thermal Stability Test (Cell Level) 4.4.3 Cycling without Thermal Management (Module and Pack Level) 4.4.4 Thermal Shock Cycling (Cell Level or Above) 4.4.5 Passive Propagation Resistance Test (Module or Pack Level) 4.5 Electrical Abuse Tests 4.5.1 Short Circuit Tests (Cell and Module or Pack) 4.5.2 Overcharge Test (Cell and Module or Pack) 4.5.3 Overdischarge (Forced Discharge) Test (Cell Level and Module) 4.5.4 Separator Shutdown Integrity Test
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Table 9-5. Outline of SAE J2929 electric and hybrid vehicle propulsion battery system safety standard – Lithium-based rechargeable cells.

1. Scope 1.1 Purpose 1.2 Future Considerations 2. References 2.1 Applicable Documents 2.2 Related Publications 3. Definitions 4. Technical Requirements 4.1 General Requirements and Considerations 4.1.1 Common Test Conditions 4.1.2 Data Collection 4.1.3 Subsystem Testing 4.1.4 Design Changes 4.1.5 Additional Observational Period 4.1.6 Safety 4.1.7 Vent System Considerations	4.2 Normal Operation 4.2.1 General 4.2.2 Vibration 4.2.3 Thermal Shock 4.2.4 Humidity/Moisture Exposure 4.3 Drop Test 4.4 Immersion Test 4.5 Mechanical Shock 4.6 Battery Enclosure Integrity 4.7 Exposure to Simulated Vehicle Fire 4.8 Electrical Short Circuit 4.9 Single Point Overcharge Protection System Failure 4.10 Single Pint Over Discharge Protection System Failure 4.11 Single Point Thermal Control System Failure 4.12 Fault Analysis 4.13 Protection against High Voltage Exposure 5. Battery System Conformance Claims and Marking 6. Notes
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Table 9-6. Hypothetical standard for Li-ion battery systems based on an outline of SAE J2579 for hydrogen vehicle fuel systems.

- DESIGN CONSIDERATIONS
 - General Safety Features
 - Hazardous Material Exposure and Toxicity
 - Automatic Fail-Safe Energy Fuel Shutoff
 - Manual Energy Fuel Shut Off
 - Management of Flammable Conditions
 - Overcharge and Overdischarge Over-pressure Protection
 - Thermal (Over-Temperature) Protection
 - Propagation mitigation
 - Fault Monitoring
 - Service Life Conditions
 - Voltage and Current Pressure
 - Temperature
 - Charging Power Fuel Quality
 - Shock, and Vibration and Crash
 - Service Life and Durability
 - Material Selection
 - Charging systems Compatibility with Hydrogen
 - Liquid Fuel Compatibility
 - Thermal Considerations
 - Corrosion and other External Effects
- DESIGN QUALIFICATION
 - Compliance with Recognized Codes, Standards, or Directives
 - Performance-based Verification
 - Verification of Performance Over Expected Service
 - Verification of Durability under Extreme Conditions and Extended Usage
 - Service Terminating Conditions
- PRODUCTION PROCESS QUALIFICATION AND VALIDATION
 - Quality Control Systems
 - Process Verification
 - Routine Production Tests (for Each Unit Produced)
 - Periodic Production Tests (Batch/Lot Tests)
- VEHICLE INTEGRATION
 - Labels
 - Installation and Mounting
 - Discharge Systems
 - External Charging and External Discharging (for maintenance and post-crash) Fueling and De-Fueling
 - Owner Guide or Manual
 - Emergency Response
 - Maintenance
 - Service Life Limitations
- REGULATORY APPROVAL

Table 9-7. Potential gaps in Li-ion battery standards.

<ul style="list-style-type: none"> • DESIGN CONSIDERATIONS <ul style="list-style-type: none"> ○ General Safety Features ○ Service Life Conditions ○ Material Selection • DESIGN QUALIFICATION <ul style="list-style-type: none"> ○ Performance-based Verification <ul style="list-style-type: none"> ▪ Verification of Performance Over Expected Service ▪ Verification of Durability under Extreme Conditions and Extended Usage ▪ Service Terminating Conditions • PRODUCTION PROCESS QUALIFICATION AND VALIDATION <ul style="list-style-type: none"> ○ Quality Control Systems ○ Process Verification ○ Routine Production Tests (for Each Unit Produced) ○ Periodic Production Tests (Batch/Lot Tests) 	<ul style="list-style-type: none"> • VEHICLE INTEGRATION <ul style="list-style-type: none"> ○ Labels ○ Installation and Mounting ○ Discharge Systems ○ External Charging and External Discharging (for maintenance and post-crash) ○ Owner Guide or Manual ○ Emergency Response ○ Maintenance ○ Service Life Limitations
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9.3 Potential Gaps in Performance-Based Design Qualification Requirements

Design qualification tests in codes and standards define a series of performance-based tests that verify the safety and durability of vehicle components, subsystems, and systems during normal service, during extremes of normal service, and during abuse. The test methods and their acceptance criteria define a minimum level of safety performance that is intended to be independent of a specific design. SAE Li-ion battery standards J2464 and J2929 define single abuse event tests, which verify that specified levels of abuse will not cause failure within a specified period of time, generally 1 hour, following the abuse. Examples include vibration, thermal shock, drop, immersion, mechanical shock, high temperature exposure, low temperature exposure, overcharge, overdischarge, and nail penetration.

Vehicles are subject to a large number of cumulative abuse events over their life. If these abuse events are not detected, and if mitigation measures are not taken before the end of vehicle life, their effects may accumulate to a level that causes unexpected and possibly hazardous failure. Current Li-ion battery standards do not appear to consider cumulative abuse events with service that are codified in performance-based design qualification requirements found in other standards. This section discusses more specific details for consideration.

9.3.1 Potential Gaps in Consideration of Damage, Damage Growth, and Damage Tolerance

Current battery standards appear to be based upon an abuse testing methodology that assumes rapid failure processes, such that if abuse does not end the life of a cell, module, or pack, it remains fully serviceable for the rest of its design life. The technical literature and analysis in Chapter 7 suggests that in-service abuse events may damage cells, modules, or packs without causing immediate or near-term failure. These abuse events or damage may not be detectable with existing controls. Furthermore, as discussed in Chapter 7 of this report, damage in cells, modules, or packs caused by abuse may grow to failure, undetected, in subsequent normal charge/discharge service duty cycles. This suggests the concern that design qualification based

only upon individual abuse testing events does not consider cumulative life cycle durability and damage tolerance that is considered in other safety standards. There appears to be a fundamental gap in Li-ion battery standards consideration of damage initiation and growth and damage tolerance.

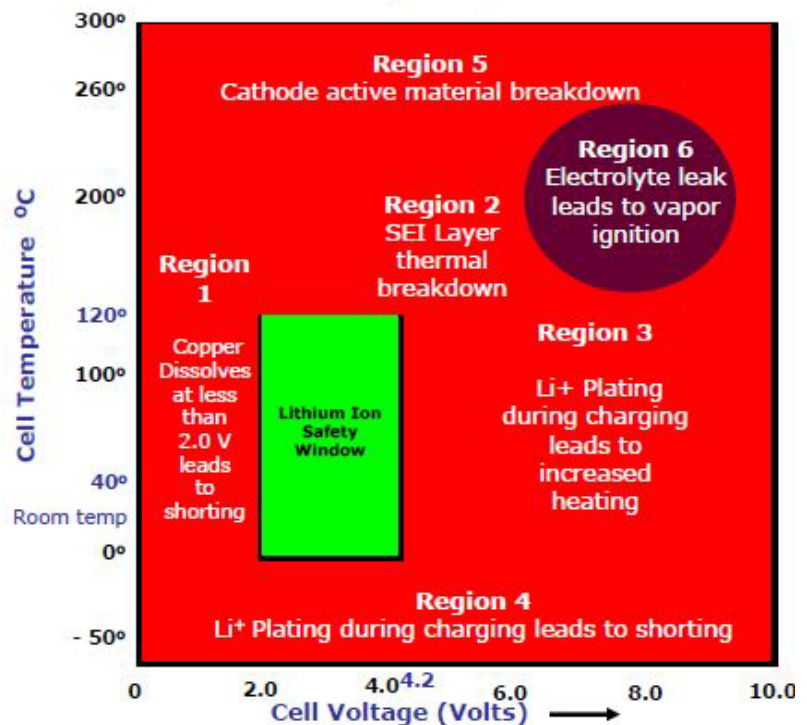
The concept of damage initiation during abuse events and growth during subsequent service loadings is well established in mechanical systems design, but appears to only be in its early stages of understanding in Li-ion battery literature. The concept of damage is leveraged here from experience with other high-energy storage systems such as hydrogen fuel tanks, which may be damaged by impacts from dropping or excessive temperature, both events that can damage Li-ion batteries and their components. The analysis of Chapter 7 supports application of this concept to Li-ion battery performance. This topic appears to be in the early stages of research and development as well as early stages of codes and standards development.

Damage is defined here as electrochemical reactions outside the range of normal charge/discharge intercalation mechanisms described in Chapter 2 of this report. Figure 9-1 from House (2007) is a simplistic illustration for this concept, which suggests that there is a safety window of cell voltage and temperature.

Outside that window, electrochemical reactions occur that are damaging, such as Li plating, copper dissolving, or SEI thermal breakdown. Chapter 7 of this report shows that the subject is more complicated than illustrated here, in that more variables influence the dimensions of the safety window and that its size and shape can vary over time. However, this illustration is instructive in highlighting the multiple mechanisms that may be considered damage and can contribute to or cause failure.

While we generally think of damage as caused by individual events, damage mechanisms such as SEI layer breakdown can be caused by electrochemical breakdown from hundreds of charge/discharge cycles in long-term service. Some Li-ion chemistries may be more prone to this type of damage than others.

The damaging reactions noted here are not reversible and can grow over time. They may grow during further excursions outside the window. In some cases, damage may grow due to normal charge/discharge operational cycles, eventually contributing to failure modes such as internal shorts.



Source: House (2007).

Figure 9-1. Simple illustration of "Safety Window" for Li-ion batteries and damaging reactions outside that window.

Damage initiation and long-term growth to failure is an important concept for development of codes and standards. It suggests that, in addition to abuse test cases, cells and batteries must be able to withstand occasional service extremes and abuse that may cause damage, but not cause immediate or near-term hazardous failure. It suggests that, if service extremes, abuse, or damage cannot be detected, then the cell or battery must be able to withstand remaining service duty cycles without failure. Alternatively, the damage must become detectable and activate systems that can mitigate or prevent hazardous failure.

This potential for damage and long-term growth indicates the need for a clearly defined service duty cycle test that represents the charge/discharge duty cycle and maximum and minimum service conditions that a cell and battery must be able to withstand. It indicates that the cell and battery should be able to withstand damaging events such as drop/impact, vibration, impact, surface damage/scratches, penetration, chemical exposure, and extreme temperatures and then be able to survive normal duty without hazardous failure for the remainder of its service life, which can be well in excess of a decade in auto service.

The concept described here is known in other fields as damage tolerance. In addition to the survival after damage, this also incorporates the concept of damage detection, which could become important as Li-ion technology grows. If the damaging reactions can be detected directly or through electrochemical models, then action can be taken by a control system to mitigate or prevent serious failure.

The next section describes application of the concept of damage and damage growth through implementation of performance-based life cycle durability requirements.

9.3.2 Potential Gaps in Life Cycle Durability Test Requirements for System Level

A cumulative damage based perspective suggests the need for life cycle durability testing, which represents cumulative abuse and service, in addition to single abuse event tests. Life cycle durability is different from performance drive cycle tests. It defines the *cumulative* extremes of service that a vehicle and battery must endure throughout the vehicle life without inducing a safety related failure. The vehicle industry has previously demonstrated the need for testing cumulative exposures to abuse followed by worst case service cycles. SAE J2579 provides an example of life cycle durability testing wherein hydrogen vehicle fuel systems are subjected to a series of abuse conditions in sequence with normal charge/discharge cycles, which is more representative of actual service. Life cycle durability is addressed in two test sequences, the Hydrogen Storage System Expected Service Performance Test and the Hydrogen Storage System Durability Performance Test.

In the System Expected Service Performance Test from SAE J2579, the hydrogen storage system must demonstrate the capability to function through cumulative exposures associated with worst-case fueling and de-fueling conditions (pressure cycling at environmental temperature limits) and parking (prolonged static pressure). This test includes the following sequence.

- Routine Production Quality Pressure Proof Test at 150 Percent of Service Pressure
- Extreme Temperature Gas Cycling: Fueling Performance
- Extended Static High Pressure Gas Test: Parking Performance
- Extreme Temperature Gas Cycling: Fueling Performance
- Extended Static High Pressure Gas Test: Parking Performance

- Gas Leak/Permeation Test
- Pressure Proof Test at 180 Percent of Service Pressure
- Residual Strength Burst Test.

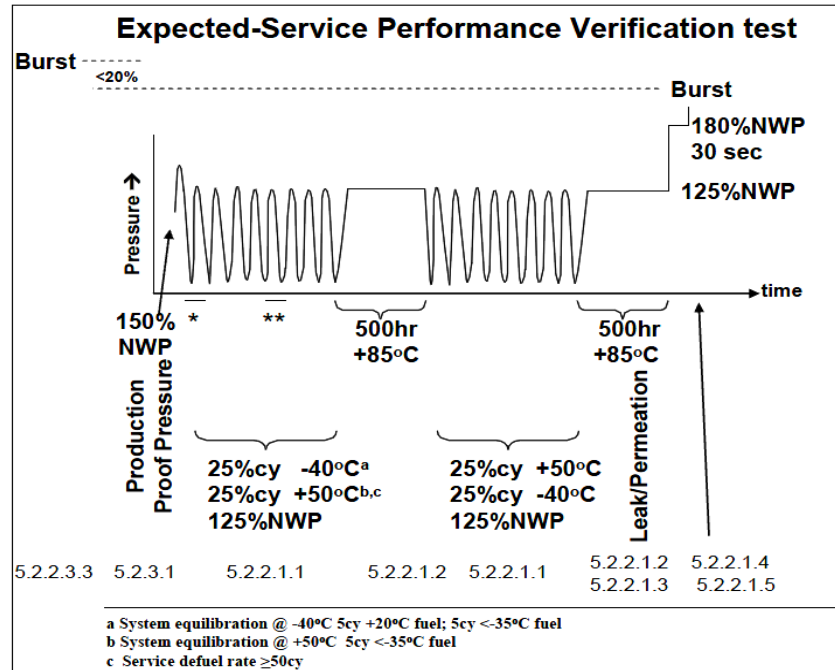
The test sequence is illustrated in Figure 9-2 from the standard. As noted earlier, cyclic pressure testing loosely corresponds to charge/discharge cycling, and parking performance at high temperature loosely corresponds to high temperature static exposure for vehicles. Both of these types of exposure can cause damage in Li-ion battery systems and are realistic to consider for in-service vehicles. Additionally, this test requires a minimum residual burst strength at the end of exposure, which implies that a battery must be able to withstand a severe charge/discharge cycle safely even after a lifetime of use.

Complementing the expected service performance test is the durability performance test, a so called “torture track” test. In this case the hydrogen storage system must survive extreme conditions and extended usage without failure. The system must demonstrate durability throughout the following sequence of exposures as illustrated in Figure 9-3.

- Routine Production Quality Tests
- Drop Test
- Surface Damage and Chemical Exposure
- Ambient Temperature Pressure Cycling Tests
- Proof Pressure Test at 180 Percent of Service Pressure
- Residual Strength Burst Test.

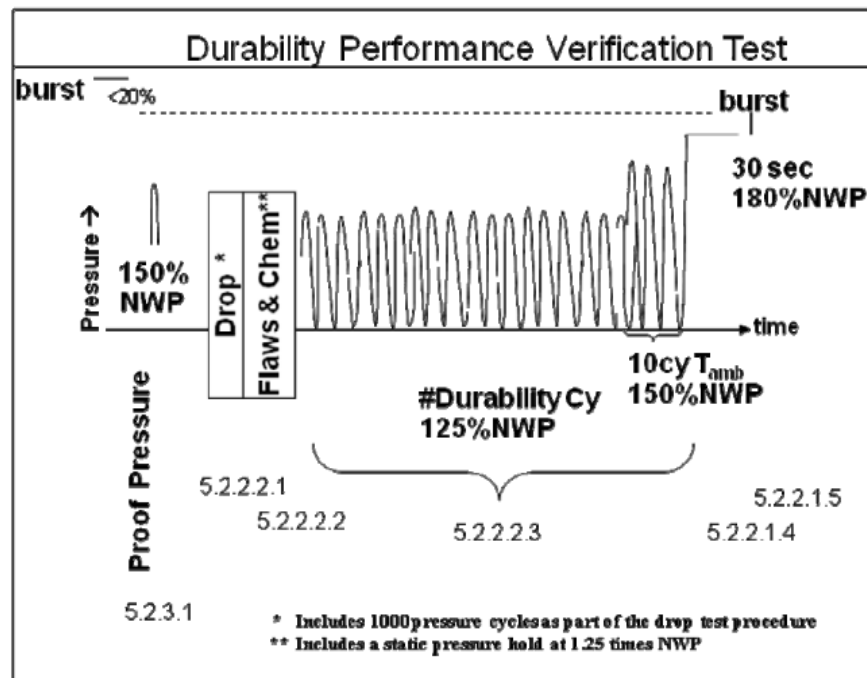
Again, this test requires a minimum residual burst strength at the end of exposure, which would suggest that a battery must be able to withstand a severe charge/discharge cycle safely even after a lifetime of abuse.

While these two examples are from another high-energy storage system, they illustrate industry practices for safety requirements following a series of lifetime events that can initiate damage and potentially cause it to grow to failure. Such a durability test does not appear to be in the current standards for Li-ion battery systems.



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Figure 9-2. Illustration of SAE J2579 expected-service performance verification test for hydrogen vehicle fuel systems.



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Figure 9-3. Illustration of SAE J2579 durability performance verification test for hydrogen vehicle fuel systems.

9.3.3 Potential Gaps in Misuse and Abuse Considerations for Durability

Li-ion battery vehicles will be subjected to the complete range of life cycle misuse and abuse that are experienced by conventional vehicles. The abuse event tests in SAE J2464 and SAE J2929 appear to have originated from abuse events known to cause failure of Li-ion battery cells. From a comprehensive systems safety viewpoint, it is important to examine and define abuse from the vehicle life cycle perspective. This approach examines the expected abuse extremes that a class of vehicles may experience throughout their life and from that, define the abuse durability requirements for the battery, its modules, arrays, and cells. All events in a vehicle's life must be considered, because events that are benign for conventional vehicles could be very harmful to Li-ion battery systems.

One plausible example of a potentially hazardous sequence of abuse events is a moderately severe vehicle crash requiring body repair. In this example, a vehicle is impacted sufficiently to cause undetected shock and internal crushing damage of cells. Following body repair, the vehicle is painted and cured in an elevated temperature paint oven, which grows the previously induced damage. Upon returning to service, the vehicle is then subjected to a series of severe charge/discharge cycles, which finally drives the damaged cells to failure. In the absence of understanding or training, mechanics and consumers will employ the same practices they have learned to use with conventional vehicles, failing to understand that they can harm Li-ion batteries.

Table 9-8 below provides a list of potential life cycle and abuse events identified in the safety analysis for this program. This list and others like it may be examined and expanded by knowledgeable personnel, and each element may be considered systematically for inclusion in single abuse event tests and for inclusion in the life cycle durability tests described in the previous section.

Table 9-8. Examples of potential life cycle misuse and abuse events.

<ul style="list-style-type: none"> - Operation <ul style="list-style-type: none"> - Vehicle start up (key on) <ul style="list-style-type: none"> - Unusual, atypical startup discharging - Starting under extreme high or low temperature conditions - Vehicle shut down (key off) <ul style="list-style-type: none"> - Unusual, atypical shutdown charging or discharging - Shut down/battery off under extreme high or low temperature conditions - Battery charging and discharging <ul style="list-style-type: none"> - BEV, PHEV full charge/discharge cycles <ul style="list-style-type: none"> - High rate battery recharge - High rate battery recharge under extreme high or low temperature conditions - BEV, PHEV, HEV regenerative braking charge/discharge cycles <ul style="list-style-type: none"> - High rate charge cycles from regenerative braking - High rate battery recharge under extreme high or low temperatures - BEV, PHEV, HEV charge/discharge cycles from supercapacitors <ul style="list-style-type: none"> - High rate battery recharge under extreme high or low temperatures - Normal drive and duty cycles <ul style="list-style-type: none"> - Normal drive and duty cycles under extreme high or low temperatures - Stop and go driving <ul style="list-style-type: none"> - Including regenerative braking - Long constant speed driving - Accelerating uphill - Decelerating downhill (regenerative braking) - Washing and Cleaning <ul style="list-style-type: none"> - Automated car washes - Aggressive cleaning agents - Extended vehicle operations <ul style="list-style-type: none"> - Extended driving under extreme high or low temperatures - Extended parking under extreme high or low temperatures - Extreme use <ul style="list-style-type: none"> - Extreme shock and vibration - Extreme drop impacts - Extreme surface damage followed by chemical exposure - Extreme fatigue and wear <ul style="list-style-type: none"> - Multiple daily full charges (taxi service) - Extreme environments <ul style="list-style-type: none"> - Service in hot environments (Arizona) - Service in hot humid environments (Florida, Houston) - Service in the mountains - Service in very cold environments (Alaska) - Service in snow and icy environments (northern U.S.) - Durability <ul style="list-style-type: none"> - Usage beyond the acceptable service life of batteries (years or duty cycles) - Minor to Moderate Accidents (battery damaging events) <ul style="list-style-type: none"> - "Fender bender" impacts - Exposure to heat or fire from nearby other vehicles or structures - Underbody impact of batteries (dragging battery on high center) - Extreme weather and temperatures <ul style="list-style-type: none"> - Extreme high ambient temperature service including battery charging and radiant heat - Extreme low ambient temperature service including battery charging - Ultraviolet light (sunlight) - Battery submerged in water (flooding) - Underbody salt and other road sprays - Soaking of battery and components in contaminant fluids due to collection in rock protection shields - Snow and ice formation <ul style="list-style-type: none"> - Packed around vehicle - Ice formed within battery compartment due to moisture intrusion - Mechanical deformation of components caused by ice formation 	<ul style="list-style-type: none"> - Mechanical Damage <ul style="list-style-type: none"> - Shipping and handling (dropping battery) <ul style="list-style-type: none"> - Dropping tools and equipment on exposed battery, controls and contacts - Abrasion from vehicle mountings, brackets and other vehicle components - Failure of mounting brackets, allowing battery/components to drop or twist - Punctures and penetrations <ul style="list-style-type: none"> - Bullets - Rocks, nails and screws - Broken frame members penetration during and after crash - Vehicle maintenance <ul style="list-style-type: none"> - Incorrectly or inadequately de-energizing batteries prior to/during maintenance - Damage batteries during removal, repair, and replacement of batteries and components - Replacement of damaged batteries with incorrect modules or arrays - Replacement of control circuit boards with incorrect components - Reflashing controls software with incorrect controls software - Lifting vehicle incorrectly, twisting and damaging mountings - Dropping vehicle off lifts - Dropping tools and heavy equipment on battery - Major body work and frame straightening - Painting <ul style="list-style-type: none"> - Sandblasting - Heating in paint curing ovens - Improper or inadequate maintenance facilities - Improperly or inadequately trained mechanics - Hacking and modification of control software by inadequately informed or trained personnel - Active Chemical Exposure <ul style="list-style-type: none"> - Exposure to active vehicle fluids (battery coolant, engine coolant, fuel cell coolant, windshield washer, gasoline, diesel fuel, hydraulic oil, sulfuric battery acids, cleaning agents, hydrofluoric acid in wheel cleaners) - Exposure to active cargo fluids in trunk or back of a pickup (acids, bases and salts: sulfuric acid, sodium hydroxide and ammonium nitrate) - Accidents and Collision (followed by repair and return to service) <ul style="list-style-type: none"> - Incorrectly or inadequately de-energizing batteries prior to towing - Lifting and towing vehicles incorrectly - Dropping tools on batteries - Penetrating battery during accident, lifting or towing - Major body work and frame straightening - Painting <ul style="list-style-type: none"> - Sandblasting - Heating in paint curing ovens - Service Terminating Conditions <ul style="list-style-type: none"> - Engulfing fire and localized fire - Gunfire penetration - Vehicle Crash - Post Service Conditions <ul style="list-style-type: none"> - Incorrectly or inadequately de-energizing batteries prior to towing - Post crash lifting and towing - Post crash storage (Junk Yard?) - Disassembly and remanufacturing of components
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9.4 *Potential Gaps in Safety Systems Integration and Testing*

As discussed throughout this report, Li-ion batteries in vehicles are integrated, complex systems. Batteries are built up systematically from electrochemical components into cells, arrays, modules, and packs. Each level of the battery has safety elements and safety controls, such as those identified in Table 9-9 below. Each of these safety elements and controls should

- Provide the intended safety function for that component,
- Complement the safety functions of adjacent components and safety functions at other levels, and
- Work together during a hazardous event to prevent hazardous or catastrophic failure.

While current Li-ion battery standards test safety functionality at some levels, there does not appear to be a systems safety perspective which defines and tests the safety functions at each level and confirms that integrated safety systems function together successfully in a variety of hazardous event sequences.

In the current and future market place it is expected that the engineering, manufacturing and integration of each component and subsystem in Li-ion batteries may be performed by a different organization and, perhaps, on a different part of the world. There is a potential for incomplete communication and understanding of safety elements and safety controls between engineers and suppliers of different components and subsystems. This introduces the potential for integration errors that may inadvertently defeat the safety components and controls of between subsystems and components.

Establishment of a comprehensive systems safety test methodology is particularly challenging, but will be important for battery systems in which engineering, integration, and manufacturing are performed by different organizations. It is also important even when all work is performed within a single organization, because communication breakdowns also occur within organizations.

Table 9-9. Examples of safety elements and safety controls at each level of a battery system from the system design in Chapters 4 and 5 of this report.

Subsystem	Safety Elements and Controls Examples
Electrochemical Components	<ul style="list-style-type: none"> • Li-ion chemistry selection • Electrolyte and additives selection • “Shutdown Separator”
Cell packaging and structure	<ul style="list-style-type: none"> • Thermal and mechanical design to control and dissipate heat including <ul style="list-style-type: none"> ○ Tab location ○ Materials and thickness of packaging • Limit/cutoff components such as <ul style="list-style-type: none"> ○ Standard and thermal fuse ○ Temperature cutoff device (TCO) ○ Protection circuit modules (PCM) ○ Positive temperature coefficient device (PTC) ○ Current interrupt device (CID) ○ Overpressure vent disc or plugs
Battery Array	<ul style="list-style-type: none"> • Cell balancing circuits to prevent overcharging weak cells • Current monitoring with power contactor trip • Array current fuse
Battery Module	<ul style="list-style-type: none"> • Power management • Thermal management • Power interlock/disconnects trip on module <ul style="list-style-type: none"> ○ Temperature ○ Current ○ Pressure
Battery Pack	<ul style="list-style-type: none"> • Power management • Thermal management • Power interlock/disconnects trip on pack <ul style="list-style-type: none"> ○ Temperature ○ Current ○ Pressure ○ Crash detection ○ Rollover detection
Vehicle	<ul style="list-style-type: none"> • Structural protection from <ul style="list-style-type: none"> ○ Shock ○ Crush ○ Penetration

9.5 Potential Gaps in Crashworthiness Requirements for Each System Level

Crash and post-crash risks are high in all vehicles due to the unpredictability and potential severity of crashes. Severe crash events induce substantial mechanical loadings on vehicles, subsystems, and components, including shock, crush, and penetration, each of which can damage or cause failure of Li-ion batteries. Crashworthiness requirements for Li-ion batteries appear to be in their early stages of development. The understanding of crash and post-crash behavior of Li-ion batteries appears to be much less than that of other high-energy density energy storage systems. Current requirements emphasize shock loadings, but additional consideration may be needed for allowable crush or allowable penetration of battery casings and housings. If battery

crush and penetration are not acceptable, then suitable requirements may need to be implemented to prevent crush or penetration in the event of a crash.

Consideration may be needed for specific crashworthiness requirements at each system level in terms of resistance to mechanical loadings including shock, crush, penetration, and abrasion. Similar to the case of integration of safety systems above, if components and subsystems are engineered, manufactured, and integrated by different organizations and, perhaps, in diverse locations, there should be clear definitions of the crashworthiness requirements for each system level and what protections higher system levels (i.e., vehicle, pack) provide to the lower system levels (i.e., arrays, cells). For example, vehicle manufacturers may depend upon the mechanical structure at the array level to provide shock protection and the casing at the module level to provide abrasion protection. If so, then design qualification tests of arrays should include shock tests and design qualification of modules should include abrasion tests.

If hazardous failure does not occur during a serious crash, there remains a potential for hazardous post-crash failure. Post-crash vehicles are likely to still have substantial energy stored on board while electronic control systems may not be operative. Furthermore, the “damage state” is unclear and the proximity of the battery to hazardous failure is unknown. If crash induced damage is severe enough, the subsequent movement, towing, or maintenance of the vehicle could cause further damage and hazardous failure at unpredictable times, with potentially serious consequences.

Dissipation of the electric charge in vehicle batteries (de-energizing) is expected to reduce the energy stored on board, thereby potentially reducing the post-crash failure hazards. However, a caution is warranted here. There is the possibility that improperly de-energizing a damaged battery may cause damage where there was none, or damage growth where it previously existed. Damaged battery cells are capable of a number of other electrochemical reactions beyond the normal charge/discharge reactions, such that de-energizing the battery may not automatically render them safe. Lithium plating causing dendrite growth is an example of a potentially hazardous reaction that could occur in a damaged battery during de-energizing, and could contribute to failure even in a depleted battery.

The results of this investigation suggest that the current understanding of crash and post-crash behavior of Li-ion batteries is much less than that of other high-energy density energy storage systems. Crash and post-crash risks are high due to the unpredictability and potential severity of vehicle crashes. It is unknown if existing crashworthiness requirements are sufficient to ensure a level of safety comparable to that of other vehicles or if further crashworthiness requirements may be appropriate and necessary. This topic is also discussed in Section **Error! Reference source not found.** Risks due to Immature Crash and Post-Crash Safety Requirements.

9.6 Potential Gaps in Quality Control Requirements

One topic heading clearly missing in the comparison of standards in Section 9.2 is quality control. SAE J2579 includes the following quality control topics, which are absent from SAE J2464 and SAE J2929.

- **PRODUCTION PROCESS QUALIFICATION AND VALIDATION**
 - Quality Control Systems
 - Process Verification
 - Routine Production Tests (for Each Unit Produced)
 - Periodic Production Tests (Batch/Lot Tests).

The discussions in Chapters 2 and 3 of this report show that Li-ion battery components are variable and sensitive to manufacturing errors and deviations. Design and manufacturing errors are identified throughout the analysis as a likely contributor to failure. Other automotive industry standards require that each system level of design and manufacturing include requirements for comprehensive and complete quality control, including nondestructive production tests on each unit and destructive testing on each batch or lot. Similar requirements would be expected to be necessary for Li-ion battery systems.

9.7 Closure

As noted in the introduction to this chapter, codes and standards are important for the industry and for NHTSA in that they define industry consensus on minimum design and test requirements to achieve a desired level of safety. The assessment conducted here suggests that codes and standards for Li-ion battery vehicle systems are in their early development stages and incomplete at this time. It is critical that codes and standards continue to develop and evolve to support development and evolution of technology, and help avoid the deployment of incompletely validated and tested designs that might harm safety and help ensure a level playing field for all developers and manufacturers. The next chapter provides specific assessments and suggestions for consideration in terms of risks and potential mitigation strategies.

9.8 References

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10 Potential Hazards, Risks, and Risk Mitigation Strategies

This chapter integrates the results of the preceding chapters of the report to summarize potential hazards, risks, and risk mitigation strategies for Li-ion battery vehicle safety identified in the program.

Li-ion batteries are an important new technology for vehicles because of their high electrical energy density storage capacity and excellent power delivery characteristics. These batteries can enable vehicle drivetrain designs with greater efficiency and reduced emissions. Li-ion batteries also allow the driving public to continue to use existing, well established gasoline and diesel fuel infrastructure and to leverage the existing electricity infrastructure and its lower cost energy. As with most advanced fuel and drivetrain technologies, Li-ion battery technology is currently more expensive than conventional technologies and substantial investment is being made to improve performance and reduce its weight and cost. The results of this investigation show that Li-ion battery technology is a rapidly evolving technology field that is far from settled.

The ability to store and deliver substantial energy onboard a vehicle also implies that substantial energy can be released, with corresponding hazards, in the case of failure. In this case, the energy is stored electrochemically in batteries, rather than chemically as a fuel. While systems safety engineering can achieve levels of safety with Li-ion technology comparable to that of conventional fuels, the automotive industry does not have decades of experience with it and the same understanding that it has concerning conventional and alternative fuels. Nor is there a directly comparable technology that can provide a strong experience base for development of safety requirements. The electrochemistry and hazards of nickel-metal hydride (NiMH) and other vehicle battery chemistries are sufficiently different that their experience base is not adequate for Li-ion battery safety assessments.

The risks associated with Li-ion battery systems derive fundamentally from the novelty of the technology and limited long-term experience base with its safety performance. Vehicle service is one of the most diverse and challenging engineering applications because of the diversity of environments, vehicle users and potential for misuse and abuse. There is limited experience in understanding how the rigors and challenges of severe vehicle duty cycles affect the long-term safety of Li-ion batteries and systems. Auto makers and battery manufacturers are working diligently to ensure that the battery systems being deployed are safe for consumers, but it is an evolving field. The same was true of natural gas and propane fuel vehicles in the 1990s and of hydrogen fuel vehicles in the 2000s.

The primary suggestion for consideration from this investigation for mitigating Li-ion battery vehicle safety risks is to encourage and support research, development, and implementation of comprehensive design qualification standards and performance-based test methodologies that ensure consumer safety, without obstructing evolution of the technology. Standards developments to date have focused on short-term failures resulting from individual abuse events. This investigation suggests that future developments should consider life cycle durability in which cumulative events and service over the life of a vehicle may initiate, grow, and cause battery failure. These developments require fundamental research on damage initiation, growth, and failure. Along related lines, the investigation also suggests that future developments should consider damage initiation during crash events and detection after crash. Little is understood about when and how damage may initiate during a crash and how subsequent lifting and towing activities could drive the damage to failure.

This chapter is intended to integrate the analyses and discussion of the previous chapters into a high-level executive summary addressing

- Fundamental causes of potentially hazardous failures,
- Hazards resulting from safety related failures, and
- Potential risks and mitigation strategies.

10.1 Mechanisms and Causes of Potentially Hazardous Failures

This section describes the fundamental failure processes and causes of failure at the electrochemistry and cell levels, which provide the bases in this report for identifying the vehicle-level events that may contribute to failure. A basic observation of this investigation is that hazardous failures begin at the electrochemistry level of Li-ion batteries, whether there is a manufacturing defect or external mechanical abuse that leads to a short circuit, or repeated intercalation induced swelling of the anode, which initiates and grows cracks, or an error in the battery management system that controls charging and discharging. There are numerous external events or processes in the life of a vehicle that could contribute to damage and failure in a Li-ion battery. The contribution of these events or processes toward failure depends upon their contribution to electrochemical processes within a battery cell or series of cells.

10.1.1 Fundamental Safety Related Damage and Failure Processes

Ultimately the design of Li-ion batteries is about building a system to manage and control the electrochemical reactions and physics in Li-ion cells to safely and efficiently receive, store, and discharge electrical energy. In the case of vehicle batteries, this is a complex multi-physics system consisting of thousands of cells. Understanding and characterization of safety of Li-ion battery systems begins with understanding and characterization of the electrochemical behavior within those thousands of cells.

Damage and failure are broad terms used in this investigation to describe complex electrochemical processes resulting from electrical, thermal, and mechanical stresses. For the purpose of this investigation, safety related *failure* occurs when electrochemical reactions within a cell become uncontrolled and self-propagating, exceeding the ability of the battery management system (passive and active) to maintain control. *Damage* is defined as irreversible electrochemical reactions outside the design charge/discharge intercalation mechanisms as well as stress induced fractures and cracks such as those caused by diffusion of the lithium into and out of the anode. Abuse and normal service charge/discharge cycles may cause damage to grow in a controlled fashion, until it becomes self-propagating and exceeds the capabilities of the battery management system. The irreversible electrochemical reactions that occur during damage and failure are exothermic and may generate gases, resulting in the buildup of excess heat and excess pressure within a cell. Furthermore, the irreversible reactions are accelerated by increasing temperature from excess heat, with the potential for thermal runaway. Compression of the electrochemical component layers in a cell due to diffusion of lithium into and out of anodes and/or external mechanical forces can also accelerate electrochemical reactions, contributing to damage and failure propagation. Cells are tightly packed together for performance and packaging reasons. Consequently, excess heating and mechanical pressure from a failing cell can induce damage and potential failure of adjacent cells. If not mitigated by safety systems, failure can propagate, uncontrolled, from cell-to-cell, achieving a catastrophic failure of an array, module, and battery system.

10.1.2 Internal Cell Failure Mechanisms

In general, the technical literature indicates that, while there are many factors, the primary parameters controlling Li-ion cell and battery performance are temperature and operating voltage. For each battery chemistry, design, and expected duty cycle, there is a range of temperatures and range of operating voltage in which electrochemistry is dominated by intercalation mechanisms described earlier. Outside this range, undesirable side reactions may occur which can lead to self-heating (exothermic reactions) and/or internal electrical shorts (excessive flow of electrons). This operating window and undesirable side reactions are discussed in more detail in Chapter 7 of this document. Exothermic reactions and/or internal electrical shorts may be triggered by manufacturing defects, or mechanical, electrical, or thermal errors, misuse or abuse (Arora, Medora, Livernois, & Stewart, 2010). If allowed to continue, these reactions or shorts can create conditions for self-heating within the cell; which grow to become uncontrolled increases in temperature and pressure (thermal runaway); and potentially end in venting or catastrophic failure of the cell. Surrounding cells may be affected by elevated temperature and pressure, and cell failure, with the potential for propagation beyond the individual cell. Internal fail-safes to protect against thermal runaway, including electrical controls, physical vents, thermal barriers, and reaction inhibitors, can be designed into the battery cell or pack to limit or prevent the effect of the external abuse on internal heating of the battery; likewise, external cooling systems are being developed to dissipate heat such that internal self-heating reaction temperatures and heating rates are managed.

10.1.2.1 Exothermic Reactions and Thermal Runaway

Perhaps best known of the potential failure mechanisms of Li-ion batteries is thermal runaway in which external short circuits, internal short circuits, cell overcharging, cell over-discharging, physical abuse such as crush, or exposure to high ambient temperatures can each potentially cause overheating of a cell and initiate thermal runaway events, or weaken the cell such that it is more prone to thermal runaway (Arora, Medora, Livernois, & Stewart, 2010; Brenier, McDowall, & Morin, 2004). Once initiated, thermal runaway is self-propagating failure within a cell, a series of cells, an array or module, or even beyond the enclosure to the vehicle. Thermal runaway is most likely to be realized when an event occurs that results in rapid heating of the cell that outpaces the rate of heat dissipation in the cell. Adiabatic self-heating can be caused by thermal (e.g., radiant heating), electrical (e.g., short circuiting), or physical (e.g., compression) external effects.

The following exothermic reactions are thought to take place during most thermal runaways in Li-ion batteries; note that not all of these events occur or occur sequentially.

- SEI layer decomposition
- Reaction of intercalated lithium with electrolyte
- Further reaction of intercalated lithium with electrolyte
- Electrolyte decomposition
- Reaction of intercalated lithium with binder
- Positive active material decomposition (and possible electrolyte combustion)
- Lithium reactions

These reactions occur when temperatures approach or exceed specific thresholds. They are exothermic in nature, thus generating more heat that contributes to further electrochemical reactions and breakdown if the heat is not dissipated.

10.1.2.2 Internal Short Circuit

Thermal and electrical causes of failure are often coupled together because an increase in one effect (i.e., power surge) typically results in an increase of the other (i.e., local heating). Internal cell short circuits result in excessive flow of electrons within the cell, increasing Joule heating and increasing temperatures, again potentially contributing to thermal runaway. Several different initiating events or physical entities have been hypothesized to lead to an internal short circuit (adapted from Arora, Medora, Livernois, & Stewart, 2010), including the following.

- Incorrect charging
 - Incorrect charging protocols for the specific battery chemistry
 - Charging occurring at temperatures above the rated temperature
 - Charging at low temperatures, which causes plating
 - Overdischarge leading to copper plating.
- Cell internal component failures
 - Failure of the separator material, particularly related to repeated cycling
 - Shrinkage of the separator allowing edge contact of the electrodes or current collectors
 - Nano-particles detaching from the electrodes
- Undesirable side reactions
 - Lithium plating
 - Growth of dendrites
- Errors in cell design and/or manufacturing
 - Improper design of the cell tabs.
 - Internal cell contaminants
- Mechanical abuse of the cell

These topics are discussed in more detail in Chapter 2 of this report.

10.1.2.3 Aging and Internal Mechanical Stress

Battery failures that lead to sub-optimal performance and degradation can often be traced back to aging mechanisms within the cell. The cathode and the anode age differently, and the majority of aging in the system takes place at the interface of the separator, the electrolyte, and the cathode or anode. Aging at either electrode can lead to a change in its properties that varies with both calendar time and use. During storage, self-discharges and increasing impedance can shorten shelf life. In addition, trace contaminants, such as water and iron, can have significant effects on the degradation. The cycle life is typically influenced by stress induced degradation and lithium metal plating.

The diffusion of the lithium into and out of the anode introduces several possible degradation paths. The intercalation of lithium into the anode results in a swelling of the anode, resulting in diffusion induced stress (Deshpande, Verbrugge, Cheng, Wang, & Liu, 2012; Renganathan, Sikha, Santhanagopalan, & White, 2010). The stress can lead to fractures and crack growth, which act to expose fresh anode surface to the electrolyte. This exposed surface then reacts with the electrolyte to form additional SEI material, further decreasing the cell's capacity. The lithium

diffusing through the existing SEI layer can also react with the SEI layer to increase its thickness, further contributing to aging and capacity fade (Deshpande, Verbrugge, Cheng, Wang, & Liu, 2012).

Several studies have explored diffusion induced stress in anodes, finding that the magnitude and orientation of the stress can lead to cracking of the electrode materials, which may lead to increased impedance of the electrodes. As discussed in Chapter 2, with references, the stress in anodes is also larger at the interface with the separator and can be affected by

- Charge/discharge rate,
- Size of the particles, and
- Morphology of the electrode.

The diffusion of lithium onto and out of the cathode can also lead to a swelling and cracking of the cathode although the magnitude of the swelling is often less than for the anode.

The swelling of the anode and cathode during charge and discharge can lead to change in dimensions (swelling) of the cell. The largest component of this change occurs during the first charge cycle, when the SEI is initially formed, but the swelling continues during the life of the cell. The repeated change in cell pressure can cause any burrs or sharp contaminants to puncture the separator (Mikolajczak, Kahn, White, & Long, 2011).

Li-ion chemistries work because Li-ions transfer back and forth and diffuse into layers between the cathode and anode as the cell is cycled. As external environmental temperatures increase or decrease, the transfer of ions is affected and cell performance is less than optimal; therefore, many commercial battery designs include cell temperature controls to prevent performance degradation.

There are many sources of internal mechanical stress that can contribute to degradation in the Li-ion battery cell, including stress induced during manufacturing from calendaring⁶ the electrodes (Yi, Wang, & Sastry, 2006), stress induced by packaging the cell (Lee, Lee, & Ahn, 2003; Wang, Sone, & Kuwajima, 2004), and stress induced by electrochemical cycling as described in the previous section (Zhang, Wang, & Tang, 2012). The mechanical stress can lead to increased surface area of the *Electrode* materials, loss of continuity in the electrodes, and a decrease in the free volume within the electrodes (Daniel & Besenhard, 2012).

Additional stress can arise in the cell due to mismatch in the thermal expansion coefficient between different electrode materials, and differences between the electrode and current collectors. The thermal changes of the cell can arise both from changes in the ambient environment and exothermic reactions or resistive heating within the cell.

It is important to point out that internal mechanical stress effects on durability differ substantially from electro-chemical effects on durability. Battery cells are a multi-physics combination of electro-chemistry, electrical, mechanical, and thermal processes that do not scale equally with any single parameter such as stress.

⁶ Calendaring an electrode is the process of running the electrode between a series of rollers to achieve uniform thickness of the *electrode* material.

10.1.3 External Causes and Contributors to Cell Failure

The results of this investigation suggest the following seven fundamental categories of failure causes for Li-ion battery cells. By one means or another, the Li-ion batteries are designed to protect against or prevent, these failure causes.

- External electrical causes such as external electrical short, overcharging, or overdischarging
- External thermal causes such as exposure to high temperatures or charging at cold temperatures
- External mechanical causes, which include excessive shock, impact, compression (crush), or penetration
- External chemical contamination, including packaging penetration by corrosive and aggressive agents and contamination of internal components by water, saltwater, or corrosive agents
- Service-induced stress and aging causes such as excess cycling that cause electrochemical component breakdown, fracture, and crack growth
- Cumulative abuse and service causes, in which sequences of electrical, mechanical, and thermal abuse, summarized above, with charge/discharge duty cycles cause damage to initiate and grow to the point of failure
- Errors in design, manufacturing, operation, and maintenance that induce electrical, mechanical and thermal abuse causes.

As noted above, at the most basic level, Li-ion battery components and subsystems are designed to accept, store and deliver electrical energy, while avoiding or mitigating these fundamental failure causes at the cell electrochemistry level.

10.1.4 High-Level Flowchart of System Failure Causation and Hazards

Figure 10-1 provides a high-level “systems” failure flowchart illustrating the relationship of system level causal factors, external cell level causal factors, internal cell damage, failure by uncontrolled heating and thermal runaway, propagation to other cells and, finally primary and secondary hazards. The figure is provided to illustrate the “funnel” of possible factors that cause damage and failure of a cell. Safety related failure generally results in uncontrolled heating and pressure rise, that, if not mitigated, damages adjacent cells and may propagate and cascade through a battery system.

As discussed in different sections throughout this report, there are multiple potential causes and contributors to safety related failure at the system level, including causes at the vehicle, battery management system, pack, module and array levels. Causes and contributors include defects, operational and service extremes, service errors, cumulative abuse and service cycles and crash and post-service errors. If these causes and contributors aren’t prevented or mitigated through design or safety protections, then they can create factors that cause damage and failure at the cell level, including electrical causes such as overcharging, thermal causes such as high temperature exposure, mechanical causes such as crush or penetration, as well as chemical contamination, service-induced stress and cumulative abuse and service cycles at the cell level.

External cell level causal factors can initiate and grow damage within the cell, such as internal short circuits (electrical), fracture and crack growth (mechanical), SEI layer decomposition

(electrochemical component breakdown), growth of dendrites (undesireable side reactions) and uncontrolled exothermic reactions.

If not prevented or mitigated, the causes and contributors to damage and failure at the cell level can result in uncontrolled exothermic reactions and heating and pressure rise within a cell, i.e. thermal runaway. If thermal runaway cannot be controlled or mitigated through measures such as thermal shutdown separators, then the cell may vent, creating local overpressure and releasing combustible solvent vapors that may ignite and burn, the primary hazards of cell failure. If pressure relief protections are not present or fail, then cells may rupture, potentially also releasing hot particles and projectiles. If the failures do not propagate beyond the cell, then these primary hazards may be contained within the casing of an array or module.

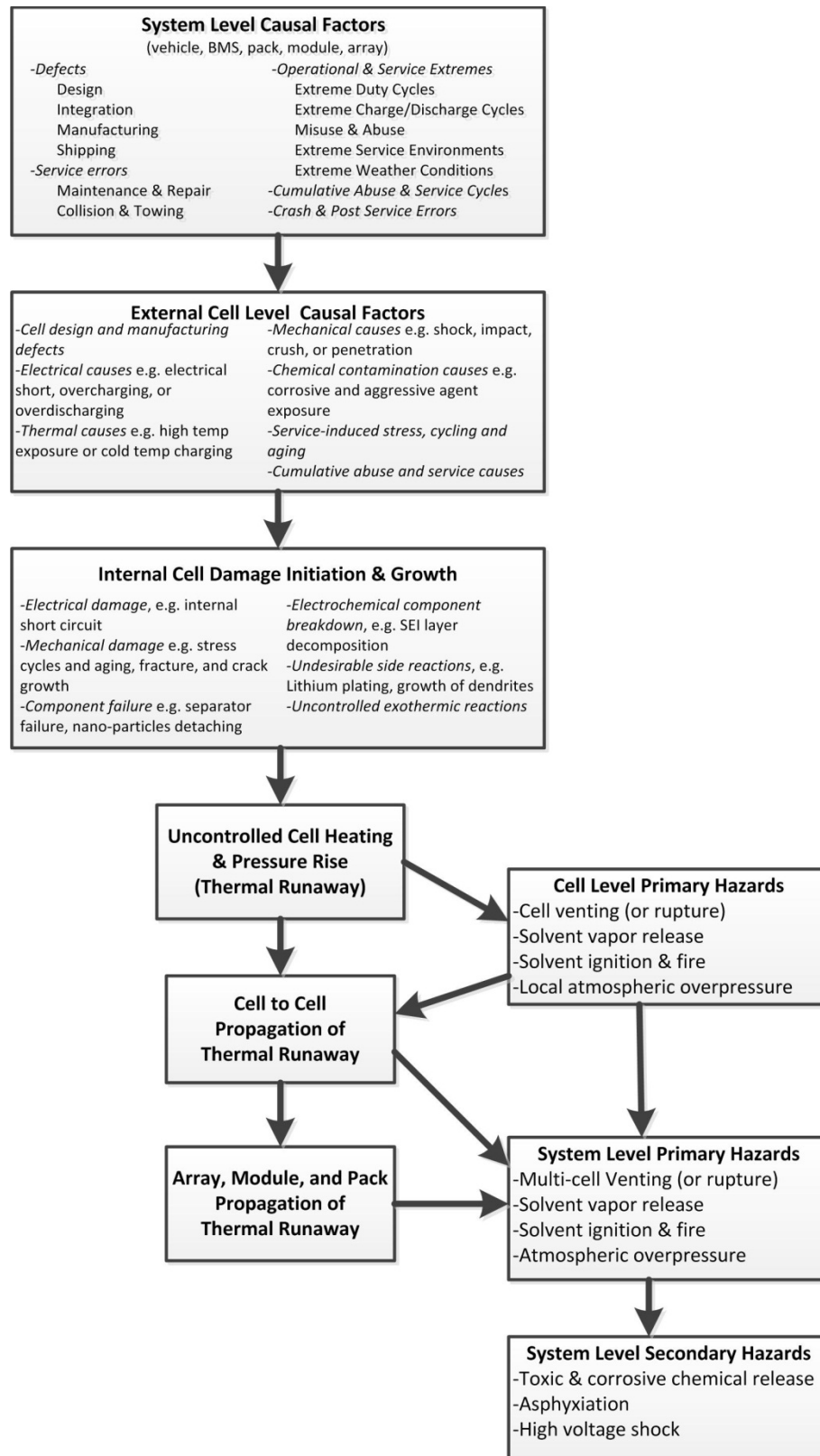


Figure 10-1. High-Level Flowchart of System Failure Causation and Hazards

Depending upon cell, array and module design, thermal runaway of a single cell can propagate by overheating, and possibly crushing, adjacent cells. Heat from combustion of venting solvent vapors may also support propagation of thermal runaway through adjacent cells.

If cell-to-cell propagation is not prevented or mitigated by safety systems, then the process has the potential to cascade through an entire array, module or possibly the entire battery pack. Failure of multiple cells increases the intensity of the primary hazards of venting, local overpressure, release of combustible solvent vapors and potential for their ignition and burning. The primary hazards have the potential to create additional secondary hazards such as release of toxic and corrosive chemicals, asphyxiation, and electrical shock hazards due to exposure of high-voltage conductors.

This figure is intended to provide a high-level view of the complex and intertwined relationships among the many factors which can cause or contribute to Li-ion battery failures and associated hazards.

10.2 Hazards Resulting From Safety Related Failures

For the purposes of this report, a hazard is the result of a failure that could lead to safety issues or consequences for vehicle passengers, first responders, and the public and surrounding property. This assessment does not consider operational hazards such as a drivetrain failing to operate while in heavy traffic. The term “hazardous failure” is used in this report to indicate one of the following hazards.

- Potential primary hazards associated thermal runaway induced heat and pressure
 - Venting of high-temperature electrolytic solvent vapors, either through pressure relief devices or holes in the casing
 - Combustion and flammability of ejected flammable electrolytic solvent vapors
 - Local atmospheric overpressure
 - Cell casing rupture and release of projectiles (If pressure relief devices are not present or if they fail)
- Potential secondary hazards that develop as a consequence of the primary hazards
 - Toxic and incompatible (corrosive) materials
 - Asphyxiation
 - Ignition and burning of adjacent flammable vehicle components or surfaces
 - High-voltage electrical shock hazards, (due to melting or burning of electrical insulation and isolators)

The heat and pressure resulting from thermal runaway, as well as combustion of solvent vapors and local overpressure may create conditions for self-heating within adjacent cells, particularly if they are damaged by the similar defects, errors, misuse or abuse that damaged the first cell. Consequently, the potential exists for propagation of thermal runaway throughout a series of cells within an array and module. The severity and consequences of particularly hazard are clearly multiplied through propagation beyond a single cell. Each is summarized below. More detail and background on each are provided in Chapters 2 and 3 of this report.

10.2.1 Primary Cell and Battery Venting and Rupture Hazards

If heat generation is allowed to outpace the rate of heat dissipation (thermal runaway), pressure could rise within a cell sufficient to open its pressure venting device, or possibly rupture the cell. Many cell designs include pressure relief devices that open in the case of overpressure to prevent excessive expansion of the cell casing and, potentially, casing rupture. Rupture is possible in the case of heat induced overpressure if pressure venting is not included in the cell design, if heat generation outpaces the vent response time, or if a pressure venting component fails or is defeated by other means. In such cases, the pressure at which rupture occurs and the nature of the rupture is dependent on the strength of the casing material at elevated temperatures.

The severity of the post-venting or post-rupture reactions will depend on the chemical state of the battery at the moment of rupture. If organic electrolyte solvent is ejected from the battery during venting or rupture, contact with nearby ignition sources (sparks or hot surfaces) can result in fuel vapor fire (“fireballs”) that may pose a significant threat to persons near the ruptured cell. Other vented materials may include additional combustible gases such as hydrogen (H₂) and carbon monoxide (CO) and toxic or corrosive materials, such as hydrofluoric (HF) acid.

Similar analysis can be made concerning the potential for venting and/or rupture at the array, module, and pack level. Heat generation greater than heat dissipation (thermal runaway) of multiple cells can cause the pressure to rise within any sealed subsystem sufficient to open pressure venting devices, or possibly rupture the subsystem.

A possible “worst-case scenario” in terms of severity in a Li-ion battery event is one in which the cell, array, module, or pack casing vents within a vehicle passenger compartment, resulting in thermal (combustion of solvents and decomposition products) and chemical (release of toxic gases and heavy metals) threats.⁷ In the case of rupture, vehicle passengers could also be subjected to physical threats (fragments from ruptured casing). Venting or rupture could produce possibly harmful overpressures. Post-venting or rupture vapor fires could have a large damage/injury radius with additional significant heat and pressure, posing a serious secondary threat to vehicle passengers and first responders. Vehicle frame and body panels would likely provide some level of protection from venting and rupture failures occurring underbody outside the passenger compartment. This is not considered a likely scenario, but is a worst-case scenario if all other design and operational protections fail.

10.2.2 Primary Combustion and Flammability and Hazards

Electrical shorts and thermal runaway can lead to generation of excess pressure within a cell. This pressure may be released through overpressure vent discs or plugs, or it can cause rupture of a cell, in either case releasing cell contents. Fire-safety issue arises in Li-ion batteries at the component level from the possibility of venting non-aqueous (organic) flammable solvents used with the lithium-based electrolytes, which could ignite if exposed to elevated temperatures or electrostatic sparks.

Several flammable or combustible chemicals are or could be present in Li-ion batteries, including those required for battery operation as well as the products of chemical reactions associated with internal failure processes within the battery. For combustion of these chemicals to occur, three elements must be simultaneously present: fuel, oxygen, and an ignition source.

⁷ In some hybrid SUVs, automobile manufacturers have placed Li-ion batteries under hardboard panels beneath the cargo section, which is open to the passenger compartment.

Premixed flames require that the fuel and oxygen exist in the vapor state and be in proper proportions, i.e., within the flammability limits. For diffusion flames, combustion is characterized by the molecular and turbulent diffusion rates of the oxygen and fuel (Glassman 1977). In either case, *local* concentrations of fuel and oxygen are critical for initiating and sustaining a combustion reaction, even in situations where *global* concentrations appear to not favor combustion. Two of the elements could be present prior to or during battery casing rupture: (1) flammable liquids, gases, hydrocarbons (liquid and solid), and metals (fuels) are either inherently present or can be formed upon failure; and (2) oxygen is available in the ambient air, or can be formed within the battery as a result of decomposition reactions associated with internal failure; however, evidence of combustion reactions occurring inside of the battery as a result of oxygen generated within the cell have not been reported to date (Mikolajczak, Kahn, White, & Long, 2011). The required ignition source could be in the form of hot surfaces, hot-metal sparks, internal battery shorts, exposed vehicle electrical wiring, or rupturing of the cell packaging. The flammable gases H_2 , C_2H_4 , C_2H_6 , and C_3H_6 are typically formed from failure processes occurring within a compromised battery, which were discussed in Chapter 2. These gases exhibit: (a) relatively high diffusivity; (b) low concentrations in the local atmosphere that approach or exceed the Lower Flammability Limit; and (c) low flash points (compared to ambient or operating temperatures). These gases should therefore be considered the most significant flammability threats; however, some form of internal failure mode must occur for these gases to form.

Flammable electrolyte solvents are inherently present in most Li-ion batteries and are required for the battery to function. These materials should also be considered a significant flammability threat, because they are always present in the battery or could degrade into potentially hazardous products; however, their threat of ignition and fire is not as severe as that of the flammable gases.

If battery chemicals that contain lithium do not decompose and are expelled during failure, they cannot be considered a flammability hazard, but could be a plausible material compatibility or toxicity threat. The lithiated carbon in a charged anode, the SEI layer, and any free lithium that might be present (due to dendrites or overcharging and plating), represent the greatest flammability threat in a Li-ion cell. While lithium is non-volatile (i.e., flash point will not be a concern), a lithiated anode will burst into flame when exposed to moist air. The reaction with water produces H_2 and as characteristic of many metals, it releases significant heat during oxidation (combustion) and ignites the H_2 .

Any flammability hazard assessment should also take into account the availability of oxygen within and outside of the cell. In battery casing failure conditions, oxygen is always available in the surrounding ambient air (at a volume percentage of 21%) and can participate in combustion reactions with expelled flammable battery materials, provided that ignition sources are present. If the casing remains intact, the probability of internally generated oxygen participating in any combustion reactions within the battery appears to be very low: evidence of such internal combustion reactions has not been reported in the technical literature (Mikolajczak, Kahn, White, & Long, 2011). For both types of combustion, it is important from a safety standpoint to take into account the global and local quantities of oxygen and flammable materials. Even if the minimum oxygen conditions are satisfied on the global level (e.g., the global concentration of oxygen within a battery is 3% by volume), this oxygen could undergo combustion reactions with fuel if some *local* concentration of oxygen is (a) mixed with a *local* concentration of fuel at

flammable proportions (for premixed combustion) or (b) allowed to diffuse into the fuel (for diffusion combustion). Therefore, both global and local oxygen and fuel concentrations should be taken into account for safety purposes and failure analyses.

10.2.3 Secondary Toxic and Incompatible Materials Hazards

Toxic materials are those battery chemicals and byproducts that are toxic or corrosive by themselves or react with other materials to produce toxic, flammable, or heat-generating chemicals. As described in Chapters 2 and 3, the main components of Li-ion batteries share common health effects, material incompatibilities, and flammability characteristics. To determine the toxicity and incompatibilities of specific chemicals, readers should refer to MSDS and other safety information.

The data in Chapters 2 and 3 indicate that the cathode component appears to pose significant toxicity risks. However, the chance of human exposure to chemicals in the cathode could be considered low because these components are solids that possess high melting temperatures. Exposure to these chemicals would require the rupture of a battery with fragmentation or vaporization of the component chemicals, which is considered unlikely.

The more hazardous chemicals inherently present in a Li-ion battery are those comprising the electrolyte salt and electrolyte solvent. In the majority of Li-ion battery designs, the electrolyte salt (LiPF_6) is dissolved in the electrolyte solvent (EC, DMC, PC, or DEC); therefore, the more likely hazard would be ejection or leakage of electrolyte fluid from the battery. The primary hazards with the electrolyte solvents are the health effects noted in Chapter 3 and the flammability hazards. The combustion of any of the electrolyte solvents would also yield water (H_2O), which may influence the degradation of the LiPF_6 salt, and the asphyxiates CO and CO_2 .

The primary hazards with the electrolyte salt LiPF_6 are health effects (noted in Chapter 3), and its incompatibility with water, which yields lithium fluoride (LiF), phosphoryl fluoride (POF_3), and hydrofluoric acid (HF) by the following reaction (Yang, Zhuang, & Ross, 2006):



If failure processes associated with thermal runaway occur within the battery, several hazardous chemicals may also be produced from various reactions. The significant hazardous products formed in these reactions include the flammable hydrocarbons (C_2H_4 ; C_3H_6 ; and C_2H_6); flammable gases and/or asphyxiates (H_2 , CO_2 , and CO); and LiF. Water can also be produced from the combustion of the electrolyte solvents, which could contribute to the formation of HF, POF_3 , and additional LiF.

The primary hazards with LiF are its toxicity if ingested or inhaled and its incompatibility with water. Contact with water can result in the formation of HF, one of the other hazardous materials discussed in Chapter 3. The primary hazards with HF are its extreme toxicity and corrosiveness and its incompatibility with metal, glass, and rubber (common vehicle materials), which subsequently release flammable hydrogen gas upon contact. Little to no data exist on the specific toxicity and incompatibility of POF_3 . POF_3 is assumed to have similar toxicity effects and material incompatibilities as POCl_3 given that both chemicals possess a halogen (chlorine or fluorine) and phosphorus.

10.2.4 Secondary Asphyxiation Hazards

The danger of asphyxiation is another concern with venting or ruptured Li-ion batteries. Asphyxiation may be a hazard in vehicle crashes when the battery casing has been compromised and there is little to no opportunity for external venting or air changeover within the vehicle (i.e., vehicle windows are in the up position and doors are closed). MSDS data for known asphyxiates state that the symptoms of asphyxiation (dizziness, nausea, etc.) can occur when oxygen levels are less than approximately 19.5 percent; levels under 8 to 10 percent can bring about rapid unconsciousness.

Chemicals that pose the highest threat of asphyxiation are the gases that are released when the battery casing is compromised and that displace the ambient vehicle air, such as H_2 , C_2H_4 , C_2H_6 , C_3H_6 , along with carbon dioxide (CO_2) and carbon monoxide (CO) produced from combustion. The threat of asphyxiation is also present for the volatile electrolyte solvents. For both the gases and solvents, the specific threat of asphyxiation is a function of the quantities of the chemicals released, their release rate, and the degree of accumulation in the vehicle. Most of the asphyxiates produced as a result of Li-ion battery failure are also flammability hazards, and can be present in both the flammability and asphyxiation ranges at the same time.

10.2.5 Secondary High-Voltage Electrical Shock Hazard

High-voltage electrical shock is a potential secondary post-crash and post-fire hazard. The high-voltage electrical bus on Li-ion battery and plug-in hybrid vehicles⁸ typically operate at a few hundred volts, well above the thresholds of 60 VDC and 30 VAC typically considered safe by electrical vehicle safety standards. (ELSA, 2010 Draft [2010]; ISO 6469-3; 2011-12-01; ISO 23273-3; 2006; GTR HFV 2011 Draft [2011]; NHTSA Response. NHTSA-2011-0107; 49 CFR 571.305 ; SAE J1766 [2005]; SAE J2344 [1998]; SAE J2578 (2009). It is well known that a crash can damage insulation and electrical protection systems. Additionally a thermal event caused by Li-ion cell or battery overheating could melt or combust electrical insulation and insulators, potentially allowing occupants, maintenance personnel or first responders direct contact with high-voltage components. This hazard is present on all high-voltage systems and is not limited to Li-ion battery vehicles.

The 60 VDC and 30 VAC safety threshold is based upon International Electrotechnical Commission Technical Standard 60479-1; 2005-07 titled Effects of Current on Human Beings and Livestock (IEC TS 60479-1) which provides a comprehensive summary of the effects of electric current on the human body and on livestock, including values of body impedance⁹ as a function of key variables.

The high-voltage bus on electric and hybrid vehicles is typically direct current. Some designs use DC to DC converters to boost or decrease the voltage at selected components. (Kimmel, Taylor, Sullivan, & Stephens, 2010, Stephens et al., 2013). DC to AC inverters are used at motors to convert to alternating current for propulsion. AC to DC converters may be used to convert

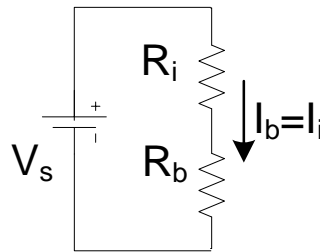
⁸ Li-ion batteries have also been observed as temporary energy storage devices on fuel cell vehicles electrical systems.

⁹ Electrical impedance is the measure of the resistance that a circuit presents to the passage of a current when an AC voltage is applied. AC impedance possesses both magnitude and phase while DC resistance has only magnitude. For the purposes of this investigation both are measured in units of ohms (Ω)

infrastructure power to DC for battery charging. High-voltage systems onboard vehicles are clearly complex.

The human body is an electrical conductor with relatively small resistance. When the body contacts an energized voltage source and return, current will flow through the body. The resulting current through the body may induce physiological effects ranging anywhere from slight pricking sensation to involuntary muscular reactions to cardiac arrest, breathing arrest, and burns. The effects and probability of ventricular fibrillation increase with magnitude of current flow and time through the body (IEC TS 60479-1; 2005-07).

In normal vehicle operation, protection from electrical shock is primarily provided by ensuring adequate “electrical isolation resistance” between the human body and voltage sources and returns. Looking at human contact as a series circuit, electrical isolation resistance ensures the resistance of electrical insulation and insulators are high enough to limit current to safe levels. This behavior is illustrated in the simple circuits in Figure 10-2. This figure compares two examples of isolation resistance R_i , and body resistance R_b , the left in a series circuit and the right in a parallel circuit.



Isolation and Body Resistance in Series

Figure 10-2. Illustration of isolation and body resistance in series.

For the isolation and body resistance in series, the current through the two resistors is the same such that

$$I_{series} = I_b = \frac{V_s}{R_i + R_b}$$

For the case where $V_s = 500V$, $R_i = 100 \Omega/V$ and $R_b = 500 \Omega$, we observe that $R_i = 500R_b$ so that the isolation resistance is substantially greater than the body resistance. Consequently in this series circuit the isolation resistance limits the body current such that it can be no greater than 10 mA ($500V/50,500\Omega$).

Electrical currents trickle through many paths in a vehicle, including insulation and insulators. Electrical isolation resistance is the composite isolation resistance of all components in the complex vehicle electrical system between high-voltage sources and the chassis and between high-voltage returns and the chassis. Based upon IEC TS 60479-1, many automotive electrical safety standards require electrical isolation of $100 \Omega/V$ for DC buses, and $500 \Omega/V$ for AC buses

or 500 Ω/V for conductively connected AD-DC buses¹⁰ (Kimmel, Taylor, Sullivan, & Stephens, 2010, Stephens et al., 2013). In those cases where the body is in series with and protected by sufficient isolation resistance, the isolation resistance is sufficient by itself to ensure body currents are within acceptable thresholds. Electrical isolation resistance is a fundamental and critical protection that limits current flow to safe levels through the body in most of the cases of direct and indirect contact with high-voltage sources.

While not specifically required in standards, high-voltage connections and components are contained within conductive electrical protective barriers that prevent direct body contact with high-voltage sources and returns during routine service and maintenance, as well as during and after crash. Components within are electrically isolated (or insulated) from conductive enclosures and barriers. Protective barriers are electrically bonded to the vehicle electrical chassis to ensure the potential of exposed surfaces are equal to the vehicle electrical chassis, thereby avoiding a voltage potential between barriers, and shock hazard if contacted by vehicle occupants, service personnel or first responders. Bonding to the chassis provides a low resistance path for current in the case where isolation resistance is lost for both voltage source and return.

NHTSA FMVSS 305 addresses high-voltage electrical shock hazards in the case of vehicle crash. Figure 10-3 and Table 10-1 summarize the key electrical safety requirements from a, 2011 revision to the standard. Following an FMVSS crash test, each high-voltage source must meet either the requirement for “absence of high voltage” (e.g. through crash activated electrical disconnects) or for electrical isolation. Absence of high voltage here requires that $V \leq 60$ VDC and $V \leq 30$ VAC. Electrical isolation for AC sources must be greater than or equal to 500 Ω/V for an AC high-voltage source. Electrical isolation for DC sources must be greater than or equal to 500 Ω/V for a DC high-voltage source *without* electrical isolation monitoring during vehicle operation or greater than or equal to 100 Ω/V for a DC high-voltage source *with* electrical isolation monitoring, during vehicle operation.

High voltages on electrical and hybrid vehicles present a serious potential hazard with possibly fatal consequences. This hazard is present on all high-voltage systems and is not limited to Li-ion battery vehicles. A substantial body of research exists on this topic and vehicle safety codes and standards appear to have achieved consensus on safety requirements.

¹⁰ Fuel cell vehicles may be unable to meet the 100 Ω/VDC requirement due to electrical current leakage through the fuel cell coolant loop. Automotive electrical standards provide alternative protections for this case.

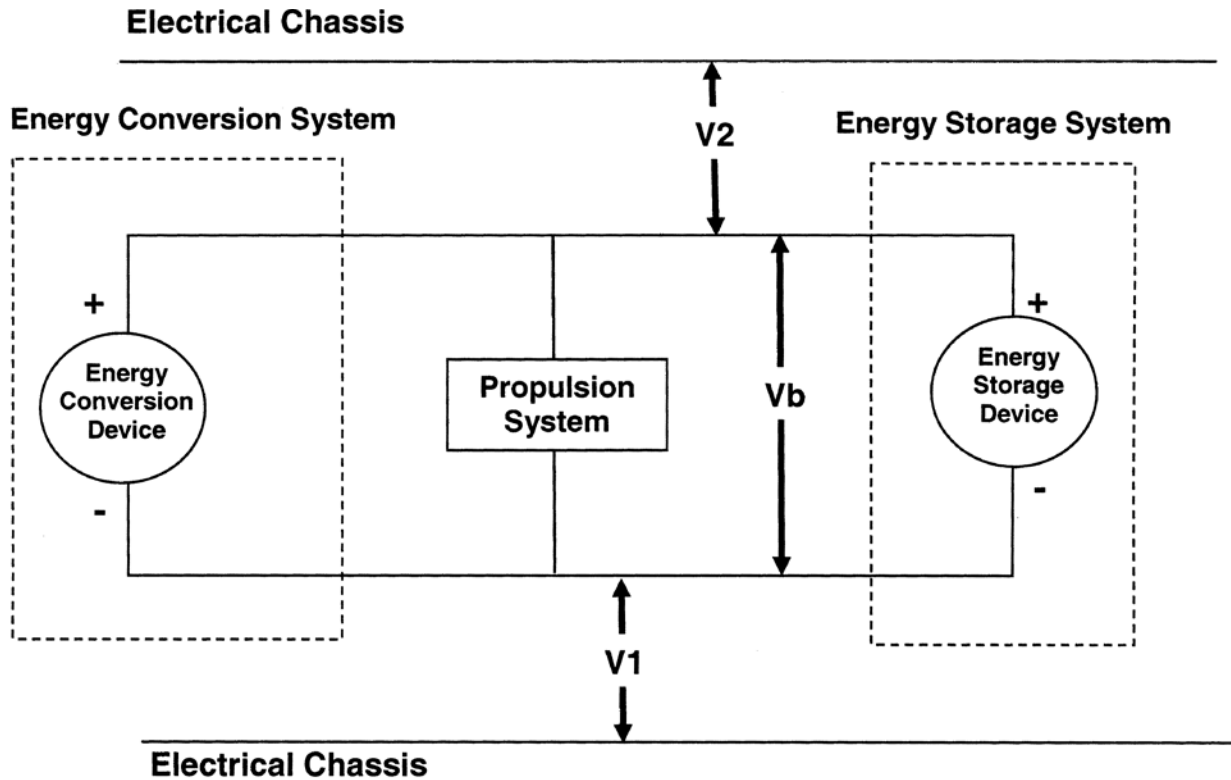


Figure 10-3. FMVSS 305 high-voltage system schematic (NHTSA 2011 Response).

Table 10-1. Summary of FMVSS 305 Electrical Safety Requirements (NHTSA 2011 Response).

	Absence of High Voltage	Electrical Isolation		
DC Sources	$V_b, V_1 \text{ \& } V_2 \leq 60 \text{ VDC}$	or	$R_i \geq 500 \text{ } \Omega/\text{V}$ for a DC high-voltage source without electrical isolation monitoring during vehicle operation	or $R_i \geq 100 \text{ } \Omega/\text{V}$ for a DC high-voltage source with electrical isolation monitoring during vehicle operation
AC Sources	$V_b, V_1 \text{ \& } V_2 \leq 30 \text{ VAC}$	or	$R_i \geq 500 \text{ } \Omega/\text{V}$	
Notes	Voltages measured according to the procedure specified in S7.7.		Isolation determined in accordance with the procedure specified in S7.6.	Isolation monitoring, in accordance with the requirements of S5.4.

R_i – isolation resistance of high-voltage source

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11 Summary of Observations and Considerations

Li-ion battery systems show great promise for automotive and other vehicular applications, and are already being used successfully in a wide range of vehicle platforms. In terms of vehicle review and inventory, the report lists more than 40 vehicle models now using Li-ion battery systems for propulsion, in experimental, concept, prototype, or full production cars. These vehicles tend to be either compact, urban-scale cars built for extremely high efficiency, or advanced performance-type cars intended to replicate conventional internal combustion (IC) sports or racing cars. As a class, the cars use between 22 and 8,000 Li-ion cells for propulsion, with battery-only operating ranges on the order of 100 miles, up to a reported maximum of 300 miles. Most of the vehicles evaluated have a top speed of 80 to 130 mph.

Automotive designers, manufacturers, and component suppliers are actively working to advance and improve the safety of Li-ion battery technology. The main failure concerns for these systems are heat dissipation, thermal runaway events, low-temperature charging conditions, crash/shock consequences, and the effects of cell stress and aging in the vehicle environment. Many fail-safe systems such as current limiting devices for charge and discharge management have been developed. The report presents idealized conceptual models of Li-ion battery modules and battery packs, showing the safety and battery management/control features and functions now available or in development.

Li-ion battery technology is in the development stage and is not yet settled. Substantial research and development is in progress to achieve greater Li-ion battery performance at lighter weight and lower cost. Researchers are exploring higher performance chemistries and are expanding the operating range of batteries through electrochemical modeling. As the technology progresses, risk increases as manufacturers attempt to obtain greater performance from existing chemistries and adopt new chemistries with less field experience. Increasing the bounds of performance implies operating the battery cells closer to limits where damage initiation and growth, leading to failure, can occur. While all manufacturers intend to deliver safe products, some may be more thorough than others, due to experience and/or resource availability. However, this does not suggest that organizational size and resource availability correlate directly to product safety.

Regarding the risk of electrochemical failure, the report concludes that the propensity and severity of fires and explosions from the accidental ignition of flammable electrolytic solvents used in Li-ion battery systems are anticipated to be somewhat comparable to or perhaps slightly less than those for gasoline or diesel vehicular fuels. The overall consequences for Li-ion batteries are expected to be less because of the much smaller amounts of flammable solvent released and burning in a catastrophic failure situation. Another safety concern is the isolation of high-voltage components to protect passengers and first responders in the event of a crash.

Li-ion electrochemistry failure processes are not self-limiting and require passive and/or active controls for management and safety. Li-ion failure processes may be understood as electrochemical or stress induced “damage” at the cell level that incubates, initiates, and grows until failure. Li-ion failure processes are time-dependent process. While failure can sometimes occur very rapidly after a cell is damaged, damage may also sometimes grow over many years and many duty cycles, causing delayed failure long after damage is initiated. Key parameters relevant to detecting and controlling damage growth are not currently measured, but are inferred through simplistic or sophisticated models.

The investigation conducted here demonstrates that there are numerous external events or processes in the life of a vehicle that could contribute to damage and failure of a Li-ion battery. Damage and failure are broad terms used in this investigation to describe complex electrochemical processes resulting from electrical, thermal and mechanical stresses. In general, the technical literature indicates that, while there are many contributing factors, the primary parameters controlling Li-ion cell and battery performance are temperature and operating voltage. For each battery chemistry, design, and expected duty cycle, there is a range of temperatures and range of operating voltage in which electrochemistry is dominated by intercalation mechanisms. Outside this range, undesirable side reactions may occur which can lead to self-heating (exothermic reactions) and/or internal electrical shorts (excessive flow of electrons). Exothermic reactions and/or internal electrical shorts may be triggered by manufacturing defects, or mechanical, electrical, or thermal errors, misuse or abuse (Arora, Medora, Livernois, & Stewart, 2010). If allowed to continue, these reactions or shorts can create conditions for self-heating within the cell; which grow to become uncontrolled increases in temperature and pressure (thermal runaway); and potentially end in venting or catastrophic failure of the cell.

For the purpose of this investigation, safety related *failure* occurs when electrochemical reactions within a cell become uncontrolled and self-propagating, exceeding the ability of the battery management system (passive and active) to maintain control. *Damage* is defined as irreversible electrochemical reactions outside the design charge/discharge intercalation mechanisms as well as stress induced fractures and cracks such as those caused by diffusion of the lithium into and out of the anode. Abuse and normal service charge/discharge cycles may cause damage to grow in a controlled fashion, until it becomes self-propagating and exceeds the capabilities of the battery management system.

Li-ion batteries are complex systems built to manage and control the electrochemical reactions in Li-ion cells to safely and efficiently receive, store, and discharge electrical energy while preventing or mitigating failure causes. The results of this investigation identified seven primary categories of external causes contributing to failure of Li-ion battery cells:

- External electrical causes such as external electrical short, overcharging, or overdischarging
- External thermal causes such as exposure to high temperatures or charging at cold temperatures
- External mechanical causes, which include excessive shock, impact, compression (crush), or penetration
- External chemical contamination including packaging penetration by corrosive and aggressive agents and contamination of internal components by water, saltwater, or corrosive agents
- Service-induced stress and aging causes such as excess cycling that lead to electrochemical component breakdown, fracture and crack growth
- Cumulative abuse and service causes in which combinations of electrical, mechanical, and thermal abuse (summarized above) and normal charge/discharge duty cycles cause damage to initiate and grow to the point of failure

- Errors in design, manufacturing, operation, and maintenance, which induce electrical, mechanical, and thermal abuse causes.

The contribution of these events or processes toward failure depends upon their contribution to electrochemical processes within a battery cell or series of cells.

For the purposes of this investigation, a hazard is the result of a failure that could lead to safety issues or consequences for vehicle passengers, first responders, and the public and surrounding property. The term “hazardous failure” is used in this report to indicate one of the following hazards.

- Potential primary hazards associated thermal runaway induced heat and pressure
 - Venting of high-temperature electrolytic solvent vapors, either through pressure relief devices or holes in the casing
 - Combustion and flammability of ejected flammable electrolytic solvent vapors
 - Local atmospheric overpressure
 - Cell casing rupture and release of projectiles (If pressure relief devices are not present or if they fail)
- Potential secondary hazards that develop as a consequence of the primary hazards
 - Release of toxic and incompatible (corrosive) materials
 - Asphyxiation
 - Ignition and burning of adjacent flammable vehicle components or surfaces
 - High-voltage electrical shock hazards, due to melting or burning of electrical insulation and isolators

The heat and pressure resulting from thermal runaway, as well as combustion of solvent vapors and local overpressure may create conditions for self-heating within *adjacent* cells, particularly if they are damaged by the similar defects, errors, misuse or abuse that damaged the first cell. Consequently, the potential exists for propagation of thermal runaway throughout a series of cells within an array and module. The severity and consequences of particularly hazard are clearly multiplied through propagation beyond a single cell.

A number of recognized safety standards are in place to govern the manufacture and use of Li-ion batteries, including those integrated into vehicles, and to document their safety under demanding environmental conditions representative of highway use. Li-ion battery standards were compared to industry standards for hydrogen vehicle fuel systems to benchmark them against a mature set of standards. The assessment conducted here suggests that codes and standards for Li-ion battery vehicle systems are in their early development stages and immature at this time. The assessment suggests there are gaps and risks inherent in new and rapidly evolving technology including the following.

- Immature design and manufacturing standards
- Immature safety systems integration requirements
- Immature quality control requirements
- Immature battery life cycle durability requirements
- Immature crash and post-crash safety requirements
- Potential for intentional and unintentional misuse and abuse.

This report emphasizes codes and standards, rather than regulation. Industry codes and standards are important for NHTSA in that they complement the FMVSS and define industry consensus on minimum design and test requirements to achieve a desired level of safety, particularly for components and subsystems. Safety codes and standards provide a basis for sharing safety knowledge, understanding, and experience across an industry as technology is evolving. They provide a consistent level of safety across the industry regardless of experience and resources. Risks in new technology development can be mitigated through the aggressive pursuit of safety codes and standards that compel industry to establish a common understanding and consensus on safety strategies. Performance-based industry standards support the continued development and evolution of technology, and avoid constraining design and innovation. Performance-based codes and standards help avoid the deployment of incompletely validated and tested designs that might reduce safety and help ensure a level playing field for all developers and manufacturers.

Some potential strategies to mitigate the risks identified in the project include the following.

- Development of codes, standards, and design qualification tests
- Development of safety systems integration standards and performance-based tests
- Development of comprehensive quality control requirements
- Development of life cycle durability requirements for each system level
- Development of crash and post-crash crashworthiness safety test requirements
- Development of standards for onboard diagnostics to prevent and mitigate misuse and abuse safety hazards
- Research to characterize cell-level damage initiation, growth, and critical size at failure
- Research to characterize cell-to-cell and array-to-array failure propagation
- Research to develop damage detection and growth interruption methods.

These strategies are consistent with conclusions and recommendations from other authors. Doughty (2012) recommends

- Improve our understanding of failure modes,
- Develop better characterization tools, and
- Improve the safety of energy storage technologies.

The potential gaps identified here do not suggest that Li-ion battery vehicles or the technology is unsafe, but that the technology is still evolving such that there is not yet an industry consensus on system design and performance-based test methodologies. Individual manufacturers are expected to conduct their own due diligence safety testing and analysis, while the industry is working to develop a consensus. Li-ion battery vehicle technology is following an evolution of technology similar to that of alternative fueled vehicles from the late 1980s forward. In this stage of technology development, designs are evolving and highly proprietary, limiting the ability of industry members to publicly discuss their knowledge and insights.

Li-ion battery technology shows great promise for enabling substantial improvements in energy efficiency in mobile and stationary applications at modest cost. The technology is in the early stages of development. As with other high energy density storage technologies, failure of a Li-ion battery may release substantial amounts of energy that may create safety hazards. The

investigation suggests that Li-ion battery safety can be managed effectively, although substantial research and development and codes and standards development is needed. In all cases, management of Li-ion battery safety requires insight, knowledge, and modeling of behavior, stress and performance at the electrochemistry level.

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Appendix A.

Survey of Li-ion Battery Vehicles

Appendix A. Survey of Li-ion Battery Vehicles

This appendix identifies vehicles using Li-ion batteries that are available or under development as of Spring 2011. The vehicles are listed and detailed first and then a brief section at the end draws observations on battery placement and chemistry.

[Editor's note: Appendix A presents numerous external sources in the form of footnotes rather than endnotes or a collected bibliography, for the reader's convenience in linking to the original information.]

The research identified more than 40 vehicles that use Li-ion batteries (Table A-1). This information was gathered from manufacturers' web sites and from a literature search of relevant technical papers, journals, and books. The summaries are organized first by level of development and then in alphabetical order by manufacturer. The four categories for level of development are:

- Experimental (not intended for production)
- Concept (to attract attention and implement new technology)
- Prototype (leading toward production)
- In Production (available on the North American market today).

Some vehicles were multiple generations of the same model or the same generic model with upgrades.

Table A-1. List of vehicles that use Li-ion batteries.

Experimental	Concept	Prototype Production	In Production
<ul style="list-style-type: none"> • Ferrari 99 HY-KERS • John Waylands White Zombie ('72 Datsun 1200 coupe) • Rolls Royce 102 EX • Venturi Buckeye Bullet 	<ul style="list-style-type: none"> • Aptera 2e • Audi eTron • BMW i8 • Cadillac Converj • Dodge EV • Lotus 414E • Porsche 918 Spyder • Subaru G4e 	<ul style="list-style-type: none"> • Ford C-Max Hybrid • Ford C-Max Energi • Jeep EV Wrangler • Fisker Karma • Mercedes-Benz S-400 • Mercedes-Benz AMG E-Cell • Ronaele Mustang 300e • Hyundai Sonata • Volvo V70 	<ul style="list-style-type: none"> • Audi A8 • BYD e6 • Chevrolet Volt • Coda • Ford Focus • Li-Motors Inizio RTX • Li-Motors Wave 2 S, SE • Li-Motors LiV Flash • Li-Motors LiV Harmony • Li-Motors LiV Wise • Mitsubishi iMiEV • Nissan Leaf • Peugeot iOn • Tata Nano • Tesla Roadster Sport • Tesla S-model • Toyota Prius • Volvo C30

The information contained in Tables A-2 through A-5 provide a summary of relevant engineering data found for each of the vehicles, including the following.

- Vehicle Specifications (years, make, model, category, class, curb weight)
- Vehicle Performance Specifications (top speed, battery-only range)
- Motor Drivetrain Characteristics (motor type, motor power)
- Vehicle Battery Specifications (type, chemistry, energy, charge, number of cells, and battery weight).

Table A-2. Specifications of Li-ion vehicles in the experimental stage.

Production Years	Vehicle Make	Vehicle Model	Vehicle Category	Class	Vehicle		Vehicle Performance Specification		Motor and Drive-train		Vehicle Battery Specifications					
					Curb Weight (lbs.)	Body Type	Top Speed (mph)	Battery only Range (mi)	Motor Type	Motor Power	Type	Chemistry	Energy (kWh)	Charge Voltage (V)	Number of Cells	Battery Weight (lbs.)
2010	Ferrari	599 HY-KERS	Experimental	HEV ¹¹		2-door										
2010	John Waylands	White Zombie (72' Datsun 1200 coupe)	Experimental	BEV	2,348 ¹²	2-door	129 ¹²	90-120 ¹²	Siamese 9' Dual armature series-wound ¹²		Lithium polymer ¹²	lithium manganese cobalt polymer ¹²	22.7 ¹²	240 ¹²	192 ¹²	
	Rolls Royce	102 EX	Experimental	PHEV		4-door	99 ¹³	120 ¹³		389 hp ¹³		Lithium nickel cobalt manganese oxide (NCM) ¹³	71 ¹³		96 ¹³	1,411 ¹³
	Venturi Buckeye	Bullet	Experimental	BEV			320 ¹⁴			600 kW ¹⁴					1,600 ¹⁴	

A-3

¹¹ www.autoblog.com/2010/03/02/ferrari-599-hy-kers-geneva-motor-show-2010/¹² www.plasmaboyracing.com/whitezombie.php¹³ www.carloversmagazine.com/index.php/2011/03/01/rolls-royce-102ex-details-released/¹⁴ www.gizmag.com/buckeye-bullet-25-world-land-speed-record/16140/

Table A-3. Specifications of Li-ion vehicles in the concept stage.

Production Years	Vehicle Make	Vehicle Model	Vehicle Category	Class	Vehicle		Vehicle Performance Specification		Motor and Drive-train		Vehicle Battery Specifications					
					Curb Weight (lbs.)	Body Type	Top Speed (mph)	Battery only Range (mi)	Motor Type	Motor Power	Type	Chemistry	Energy (kWh)	Charge Voltage (V)	Number of Cells	Battery Weight (lbs.)
2009	Aptera	2e	Concept	BEV	1,500 ¹⁵	2-door		100 ¹⁵		100 hp (75kW) ¹⁵		Lithium iron phosphate ¹⁵	10-13 ¹⁵			
2009 ¹⁶	Audi	eTron	Concept	BEV	3,527 ¹⁶	2-door	124 ¹⁶	154 ¹⁶	Four motors ¹⁶	313 hp (230kW) ¹⁶	Li-ion		42.4 ¹⁶			1,036 ¹⁶
2014	BMW	i8	Concept	PHEV		2-door	155 ¹⁷	34 ¹⁷	Internal combustion and an electric motor ¹⁷	328 hp ¹⁷	Li-ion polymer ¹⁷					
	Cadillac	Converj	Concept	PHEV		2-door	100 ¹⁸	40 ¹⁸					16 ¹⁸		220 ¹⁸	
2009 ¹⁹	Dodge	EV	Concept	BEV		2 door	120 ¹⁹			268 hp ¹⁹	Li-ion prismatic ¹⁹	Nanophosphate ¹⁹		110V and 220V ¹⁹		
	Lotus	414E	Concept	HEV		2-door		35 ²⁰	Twin motors ²⁰	204 hp (152kW) ²⁰	Lithium polymer ²⁰		17 ²⁰			
	Porsche	918 Spyder	Concept	PHEV	3,300 ²¹	2-door	200 ²¹		3.4 V8 engine ²¹	500 hp (370kW) ²¹	Li-ion					
2007 ²²	Subaru	G4e	Concept	BEV		4-door		120 ²²		(65kW) ²²	Li-ion (Laminated) ²²					

¹⁵ www.gizmag.com/aptera-2e-specification-released/10903/¹⁶ www.gizmag.com/the-audi-e-tron-electric-quattro-with-4500-nm-of-torque/12836/¹⁷ http://beta.kbb.com/car-news/all-the-latest/2014-bmw-i8-spyder-testing-in-the-snow?ref=www.google.com/search?q=2014+bmw+i8+spied+testing&rls=com.microsoft:*&ie=utf-8&oe=utf-8&startindex=&startpage=1&rlz=1i7msn_en¹⁸ http://autoshow.autos.msn.com/autoshow/detroit2009/Article.aspx?cp-documentid=16110514¹⁹ www.nytimes.com/2009/01/13/automobiles/autoshow/dodge-circuit-ev.html²⁰ www.lotuscars.com/news/en/lotus-414e-hybrid²¹ www.dreamroad.us/concept-car-the-porsche-918-spyder-hybrid/²² http://en.wikipedia.org/wiki/Subaru_G4e

Table A-4. Specifications of Li-ion vehicles in the prototype stage.

Production Years	Vehicle Make	Vehicle Model	Vehicle Category	Class	Vehicle		Vehicle Performance Specification		Motor and Drive-train		Vehicle Battery Specifications					
					Curb Weight (lbs.)	Body Type	Top Speed (mph)	Battery only Range (mi)	Motor Type	Motor Power	Type	Chemistry	Energy (kWh)	Charge Voltage (V)	Number of Cells	Battery Weight (lbs.)
2013 ²³	Ford	C-Max Hybrid	Prototype	PHEV		4-door		30 ²³			Li-ion	Lithium and manganese oxides ²³				
2013 ²⁴	Ford	C-Max Energi	Prototype	BEV		4-door		100 ²⁴	Atkinson cycle ²⁴		Li-ion	Lithium and manganese oxides ²⁵		120 and 240 ²⁴		
2010	Jeep	EV Wrangler	Prototype	HEV		4-door		40 ²⁶	Internal combustion engine Battery and electric motor ²⁶	268 hp (200kW) ²⁶						
2012	Fisker	Karma	Prototype	PHEV	4,000 ²⁷		125 ²⁷	50 ²⁷	Turbo charged, direct injected inline-4 ²⁷	255 hp ²⁷	Li-ion		20 ²⁷	110 and 220 ²⁷	315 ²⁸	
	Mercedes-Benz	S-400	Prototype	HEV	4,474 ²⁹		155 ²⁹			295 hp ²⁹						
2013	Mercedes-Benz	AMG E-Cell	Prototype	BEV		2-door		100 ³⁰	Four motors ³⁰	526 hp ³⁰					324 ³⁰	
	Ronaele, Inc	Mustang 300e	Prototype	BEV		2-door	130 ³¹	100-125 ³¹		550 hp ³¹		Lithium iron phosphate ³¹				
2011	Hyundai	Sonata	Prototype	HEV		4-door		74 ³²	Electric motor and Theta II 2.4 liter engine ³²	206 hp ³²	Lithium polymer ³²					95.9 ³²
2012	Volvo	V70	Prototype	PHEV		4-door	80 ³³	31 ³³	Diesel; permanent-magnet AC motor ³⁴		Laminated Li-ion	lithium manganese oxide ³⁵	11.3 ³³	220 ³³		

²³ www.4evriders.org/2010/09/usa-fords-electric-vision-new-hybrids-700-mile-range-phev-by-2012/²⁴ http://newautocars.org/2013-ford-c-max-energi/²⁵ http://prsync.com/batteryfast/-by-batteryfastcouk-lithium-battery-news-global-development-for-lithium-battery-manufacturing-114380/²⁶ www.automobilemag.com/green/news/0901_2010_jEEP_wrangler_unlimited_ev/index.html²⁷ www.insideline.com/fisker/karma/2012/2012-fisker-karma-first-drive.html²⁸ www.windingroad.com/articles/reviews/driven-2012-fisker-karma/²⁹ www.mbusa.com/mercedes/vehicles/explore/performance/class-S/model-S400HV³⁰ www.wired.com/autopia/2010/06/mercedes-amg-sls-e-cell/#³¹ www.greencar.com/articles/fast-times-mustang-300e-electric-musclecar.php³² www.hyundaiusa.com/sonata-hybrid/specifications.aspx³³ www.telegraph.co.uk/motoring/carreviews/6438513/Volvo-V70-plug-in-hybrid-review.html#³⁴ www.popularmechanics.com/cars/reviews/hybrid-electric/4334201³⁵ www.ener1.com/?q=content/enerdel-design

Table A-5. Specifications of Li-ion vehicles in production.

Production Years	Vehicle Make	Vehicle Model	Vehicle Category	Class	Vehicle		Vehicle Performance Specification		Motor and Drive-train		Vehicle Battery Specifications					
					Curb Weight (lbs.)	Body Type	Top Speed (mph)	Battery only Range (mi)	Motor Type	Motor Power	Type	Chemistry	Energy (kWh)	Charge Voltage (V)	Number of Cells	Battery Weight (lbs.)
2010	Audi	A8	Production	HEV	4,156 ³⁶	4-door	146 ³⁶			245 hp (180 kW) ³⁶						
2011 ³⁷	BYD	e6	Production	BEV	4,453 ³⁷	5-door	87 ³⁷	186 ³⁷	One or two permanent magnet synchronous motors ³⁷	101 hp (75kW) ³⁷		Lithium iron phosphate ³⁷	18 ³⁷			
2010-present ³⁸	Chevy	Volt	Production	PHEV		4-door	100	40	1.4L DOHC I-4 drive motor ³⁸	149 hp (111 kW) ³⁸	Li-ion	Lithium manganese spinel ³⁹	16 ³⁸	120 and 240 ³⁸	288 prismatic ³⁸	435 ³⁸
2010	Coda		Production	BEV	3,682 ⁴⁰	4-door	80 ⁴⁰	119 ⁴⁰		134 hp (100kW) ⁴⁰		Lithium iron phosphate ⁴⁰	33.8 ⁴⁰	220 ⁴⁰	728 ⁴⁰	
2011 ⁴¹	Ford	Focus	Production	BEV		4-door		100 ⁴¹		141 hp (105kW) ⁴¹	Li-ion		23 ⁴¹	120 and 240 ⁴¹		300 ⁴¹
2010 - present	Li-Motors	Inizio RTX	Production	BEV	3900 ⁴²	2-door	170 ⁴²			290kW ⁴²			80 ⁴²		24 ⁴²	
2010 - present	Li-Motors	Wave 2 S, SE Model	Production	BEV	2,350 ⁴³	4-door	90 ⁴³	200 ⁴³			Flat thin prismatic lithium polymer batteries ⁴³		40.32 ⁴³	110 and 220 ⁴³	12 ⁴³	
2010 - present	Li-Motors	LiV Flash	Production	BEV	2,700 ⁴⁴	2-door	80 ⁴⁴	120 ⁴⁴	3- phase, brushless A/C motor ⁴⁴					110-120or 220-240 ⁴⁴		550 ⁴⁴
2010 - present	Li-Motors	LiV Harmony	Production	BEV			80 ⁴⁵	120 ⁴⁵								

³⁶ www.autoguide.com/auto-news/2010/03/geneva-2010-audi-a8-hybrid-debuts-with-2-0-tfsi-engine-lithium-ion-battery.html³⁷ http://en.wikipedia.org/wiki/BYD_e6³⁸ <http://gm-volt.com/full-specifications/>³⁹ www.popsci.com/cars/article/2011-01/gm%E2%80%99s-new-battery-chemistry-it%E2%80%99s-already-chevy-volt⁴⁰ www.codaautomotive.com/all-electric-car/⁴¹ <http://reviews.carreview.com/blog/first-impressions-2012-ford-focus-ev/>⁴² www.Li-ionmotors.com/INIZIO/features.php?sub=performance⁴³ www.Li-ionmotors.com/WAVEII/⁴⁴ www.Li-ionmotors.com/vehicles/cars/flash/⁴⁵ www.Li-ionmotors.com/vehicles/cars/harmony/

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Production Years	Vehicle Make	Vehicle Model	Vehicle Category	Class	Vehicle		Vehicle Performance Specification		Motor and Drive-train		Vehicle Battery Specifications					
					Curb Weight (lbs.)	Body Type	Top Speed (mph)	Battery only Range (mi)	Motor Type	Motor Power	Type	Chemistry	Energy (kWh)	Charge Voltage (V)	Number of Cells	Battery Weight (lbs.)
2010 - present	Li-Motors	LiV Wise	Production	BEV			80 ⁴⁶	120 ⁴⁶								
2010-present ⁴⁷	Mitsubishi	iMiEV	Production	BEV	2380 ⁴⁷		82 ⁴⁷	100 ⁴⁷	Permanent magnet synchronous ⁴⁷	63hp ⁴⁷	Li-ion	Lithium manganese-oxide ⁴⁷	16 ⁴⁷	120 and 240 ⁴⁷	22 ⁴⁷	397 ⁴⁷
2010-present ⁴⁸	Nissan	Leaf	Production	BEV	3,354 ⁵⁰	5-door	90 ⁴⁸	100 ⁴⁹	Synchronous AC motor	110 hp (80kW) ⁴⁹	Li-ion (Laminated) ⁴⁸	Lithium-ion manganese ⁴⁹	24	110 and 220 ⁵⁰	192 ⁵¹	440 ¹⁵
2009-present ⁵²	Peugeot	iOn	Production	BEV		4-door	81 ⁵²	93 ⁵²	Permanent magnet neodyme synchronous ⁵²	268 hp ⁵²	Li-ion	Lithium manganese-oxide ⁵²	16k ⁵²	110 and 220 ⁵²	88 ⁵²	348 ⁵²
2010-present ⁵³	Tata	Nano	Production	BEV	1400	4-door	80 ⁵³	100 ⁵³	2 cylinder SOHC ⁵³		Li-ion	Super Polymer Lithium-ion ⁵³	12k ⁵³	240 ⁵³		
2008-present ⁵⁴	Tesla	Roadster Sport	Production	BEV		2-door		245 ⁵⁵	3-phase, 4-pole electric motor ⁵⁶	288 hp (215kW) ⁵⁶	Li-ion		53 ⁵⁶	110 and 220 ⁵⁶	6800 ⁵⁷	
2012-present	Tesla	S	Production	BEV	4,647	4-door	125	300	4-pole AC induction	40, 60, or 85 kWh	Li-ion	Nickel-based	40, 60, or 85 kWh	110, 220, J1772	7000-8000 ⁵⁸	1200
2010-present ⁵⁹	Toyota	Prius	Production	PHEV				13 ⁵⁹	Permanent magnet synchronous motor ⁵⁹	80 hp (60kW) ⁵⁹				110 and 220 ⁵⁹		330 ⁵⁹

⁴⁶ www.Li-ionmotors.com/vehicles/cars/wise/⁴⁷ www.insideline.com/mitsubishi/i-miev/first-drive-2010-mitsubishi-i-miev-plug-in-electric.html⁴⁸ www.allcarselectric.com/blog/1033880_2011-nissan-leaf-specs⁴⁹ www.examiner.com/green-transportation-in-national/turning-over-the-nissan-leaf-to-look-inside⁵⁰ http://en.wikipedia.org/wiki/Nissan_Leaf⁵¹ www.allcarselectric.com/blog/1033880_2011-nissan-leaf-specs⁵² www.peugeot.co.uk/Resources/Content/brochures/technical/peugeot-ion-prices-and-specifications.pdf?model=ion⁵³ www.evscroll.com/Tata_Nano_EV.html⁵⁴ http://en.wikipedia.org/wiki/Tesla_Roadster⁵⁵ www.teslamotors.com/goelectric/charging⁵⁶ www.teslamotors.com/roadster/specs⁵⁷ The Tesla Roadster Battery Systems Tesla Moors August 16, 2006, Gene Berdichevsky, Kurt Kelty, JB Straubel, Erik Toomre⁵⁸ http://webarchive.teslamotors.com/display_data/Spec_ModelS_US.pdf⁵⁹ www.toyota.com/upcoming-vehicles/prius-plug-in/

Production Years	Vehicle Make	Vehicle Model	Vehicle Category	Class	Vehicle		Vehicle Performance Specification		Motor and Drive-train		Vehicle Battery Specifications					
					Curb Weight (lbs.)	Body Type	Top Speed (mph)	Battery only Range (mi)	Motor Type	Motor Power	Type	Chemistry	Energy (kWh)	Charge Voltage (V)	Number of Cells	Battery Weight (lbs.)
2010-present ⁶⁰	Volvo	C30	Production	BEV		2-door	81 ⁶⁰	93 ⁶⁰		111hp (82kW) ⁶¹	Li-ion (laminated)	Lithium manganese-oxide	24 ⁶²	230 ⁶⁰	400 ⁶³	

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⁶⁰ www.topspeed.com/cars/volvo/2010-volvo-c30-bev-ar79267.html

⁶¹ www.motortrend.com/auto_shows/detroit/2010/0912_volvo_c30_bev/index.html

⁶² <http://ceramics.org/ceramictechtoday/energy-environment/volvos-electric-sexy-stunning-swedish/>

⁶³ www.swedespeed.com/artman2/publish/Technical_Features/Volvo_Tech_We_Tour_the_Enerdel_Battery_Factory_Sup_1751.html

Table A-2 shows how many plug-in hybrid electric vehicles, hybrid electric vehicles (HEVs), and battery electric vehicles are using Li-ion batteries as their source of power. The large majority of these vehicles use a lithium manganese based battery chemistry. The number of Li-ion battery cells used in each vehicle could range from 22 to 8000. The wide range is dependent on battery size, battery power needed, and the type of cell being used (prismatic or pouch), which is discussed in a prior chapter.

As shown in Table A-2, the battery-only range could be as low as 13 miles for an HEV and as high as 245 miles for a BEV. The energy stored by the Li-ion battery packs in these vehicles range from 10 to 80 kWh. The Aptera 2e concept vehicle is on the low end of the spectrum at 10 kWh, while the INIZIO RTX holds the maximum energy storage at 80 kWh.

One of the first PHEVs mass produced and sold in North America was the Chevrolet Volt, with a battery-only range of 40 miles. Since then, national and international competitors have introduced Li-ion batteries in vehicles such as the Toyota Prius, Ford Focus, and Nissan Leaf, all of which will be sold in North America.

The remainder of this appendix presents brief descriptions of individual PHEV and HEV Li-ion battery vehicles. The descriptions are meant to give a very general overview of the vehicles with include battery-specific information, a photograph or illustration of the vehicle and its battery, and information related to crash characteristics if available. Due to the rapid evolution of Li-ion vehicles, many elements are highly proprietary; therefore information presented here represents only that information that is available in published literature and manufacturers' web sites.

A.1 Experimental Vehicles that Use Li-ion Batteries

Ferrari 599 HY-KERS

Ferrari is studying applications of hybrid technology in combination with a high-performance sports car. The Ferrari 599 HY-KERS is an experimental vehicle to advance and give insight to Ferrari. To provide instantaneous torque while in motion, the electric motor cuts in during acceleration, but the hybrid system can perform in full-electric drive-train. They also use a regenerative brake system called the Ferrari Kinetic Energy Recovery System.

Component Location – Ferrari uses flat Li-ion battery cells positioned below the floor-pan of the vehicle.

www.autoblog.com/2010/03/02/ferrari-599-hy-kers-geneva-motor-show-2010/

www.zercustoms.com/news/Ferrari-599-GTB-HY-KERS.html



John Waylands White Zombie

The White Zombie is a 1972 Datsun 1200 coupe converted into an all electric vehicle making use of Li-ion batteries to provide power for the electric motor. John Wayland is the creator and has been racing his vehicle for more than 10 years. The top speed on this vehicle is 129 mph with a range of about 90 miles solely on electric drive. The White Zombie has been labeled by many as the world's quickest street legal electric car.

Component Location – The Li-ion battery packs are located in the trunk of the vehicle.

www.plasmaboyracing.com/events.php



Rolls-Royce 102EX

Two electric motors replace the V12 6.75-litre petrol six speed auto engine in the battery electric Rolls-Royce 102 EX. The Li-ion battery used for this vehicle is one of the largest battery packs fitted to a road car. The NCM battery chemistry holds around 230Wh/kg; this high energy density is important in achieving an acceptable range between re-charge. “The 102EX’s battery pack contains five modules of cells, a 38-cell module, a 36-cell module, and three smaller modules of ten, eight, and four arranged in the shape of the original engine and gearbox assembly.”

Component Location – The Li-ion battery pack and two electric motors are mounted on the rear sub-frame.

www.carloversmagazine.com/index.php/2011/03/01/rolls-royce-102ex-details-released/



Venturi Buckeye Bullet 2.5

The Venturi Buckeye Bullet 2.5 is an electric land-speed racer. This all electric experimental vehicle is capable of obtaining a top speed of 320 mph. The Bullet 2.5 is powered by a 600+ kW A123 Systems Li-ion battery pack.

Component Location – Not available.

A.2 Concept Vehicles

Aptera 2e

There is little information available about the Aptera 2e, but it is known that the 2e electric motor power output could be in the range of 100 hp (75kw) at over 13,000 rpm. This electric vehicle is powered by a lithium iron phosphate battery pack.

Component Location – Not available.



www.gizmag.com/aptera-2e-specification-released/10903/picture/66007/

Audi E-tron

The Audi E-tron was designed with four asynchronous motors allowing this sports car to accelerate from 37 to 74 mph in 4.8 seconds. The motor produces a total output of 230 kilowatts (313 hp). “The torque flows selectively to the wheels based on the driving situation and the condition of the road surface, resulting in outstanding traction and handling.” This car can be charged while stationary or in motion. Kinetic energy is converted into electrical energy used to power the onboard electrical system. This concept vehicle is a platform for Audi to learn about and produce the most efficient electric car.

Component Location – For optimal center of gravity and load distribution the Li-ion battery pack is located directly behind the passenger seat.



www.gizmag.com/the-audi-e-tron-electric-quattro-with-4500-nm-of-torque/12836/

BMW i8

An electric motor unit energized by a Li-ion-polymer battery pack powers the front wheels allowing the vehicle to travel at a top speed of 155 mph as well as travel up to 30 miles on a single battery charge.

Component Location – Not available.

www.kbb.com/car-news/all-the-latest/2014-bmw-i8-spied-testing-in-the-snow

www.bmwblog.com/2011/03/11/spy-videos-bmw-i8/



Cadillac Converj

The Cadillac Converj uses a Voltec electric propulsion system that is made up of a 16-kWh. The battery used is T-shaped somewhat resembling to the Li-ion battery used for the Chevy Volt.

Very similar if not the same drive-train. The Voltec technology consist of a combination of an electric motor and a flex fuel capable four-cylinder engine-generator and converts electrical energy from the battery or the engine-generator into mechanical energy to drive the front wheels. Combination of an electric motor and a flex fuel capable four-cylinder engine-generator.

Component Location – Not available.

<http://autoshow.autos.msn.com/autoshow/detroit2009/Article.aspx?cp-documentid=16110514>

2009 Dodge Circuit EV

The Dodge Circuit EV does not consume any gasoline and does not have any tailpipe emissions. The body style is similar to the Dodge Viper but there is no engine. The electric motor, powered by the Li-ion batteries, provides 268 horsepower traveling up to 120 mph.

Component Location – The battery pack appears to be located in the rear of the vehicle.



www.nytimes.com/2009/01/13/automobiles/autoshow/dodge-circuit-ev.html
www.google.com/imgres?imgurl=www.caranddriver.com/var/ezflow_site/storage/images/media/images/2011-dodge-circuit-ev-embedded-image-hatch-open/2686725-1-eng-US/2011-dodge-circuit-ev-embedded-image-hatch-open_articleimage.jpg&imgrefurl=www.caranddriver.com/reviews/car/09q2/2011_dodge_circuit_ev-first_drive_review&usq=Y4rewi-eHNJlsX60hG0MokfpmYw=&h=274&w=450&sz=46&hl=en&start=25&zoom=1&itbs=1&tbnid=hf8izJWZYDZTnM:&tbnh=77&tbnw=127&prev=/search%3Fq%3DDodge%2BCircuit%2BEV%2BBattery%2BLocation%26start%3D20%26hl%3Den%26sa%3DN%26rls%3Dcom.microsoft%3D%26rlz%3D117RNSN_en%26ndsp%3D20%26tbn%3DDisch%26prmd%3Ddivns&ei=EWScTan3F4rdgQfy0ozABw

Lotus 414E

This high-performance hybrid concept vehicle was displayed at the Geneva Motor Show, showcasing developments in plug in, range-extended electric propulsion, new electronic technologies to enhance driver involvement, and the Lotus Versatile Vehicle Architecture. The Lotus 414E is equipped with twin electric motors that total 408 hp and 590 lb-ft of torque and a 1.2 liter, three cylinder engine, allowing the vehicle to travel more than 300 miles. The electric only range is 35 miles. Another unique aspect of this vehicle is that the engine has the capability to run on alcohol-based fuel.

Component Location – Not available.

www.lotuscars.com/news/en/lotus-414e-hybrid
www.autoweek.com/article/20100225/geneva/100229930



Porsche 918 Hybrid Concept

This vehicle is the first plug in hybrid from Porsche. The Porsche 918 has 3 electric motors powered by Li-ion batteries propelling the vehicle to a top speed of 200 mph. The Li-ion battery can be recharged by the engine and by regenerative braking.

Component Location – The energy storage is a liquid-cooled Li-ion battery behind the passenger compartment.



www.dreamroad.us/concept-car-the-porsche-918-spyder-hybrid/

Subaru G4e

The Subaru G4e seats five passengers because of its unique shape. This battery electric vehicle uses a laminated Li-ion battery pack allowing this vehicle to travel 120 miles on battery-only.

Component Location – Not available.

<http://autoshow.autotrader.ca/2009/02/13/subaru-g4e-concept/>
http://en.wikipedia.org/wiki/Subaru_G4e

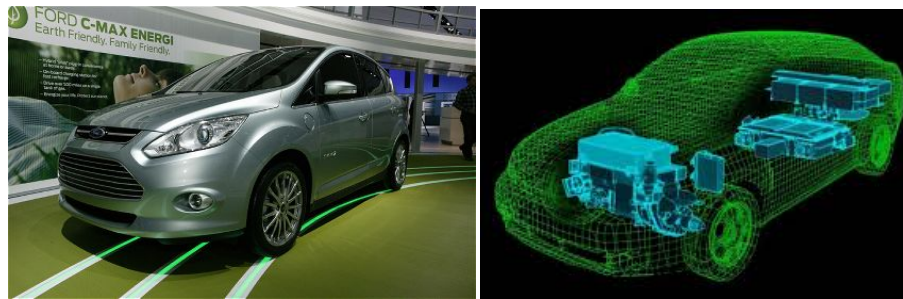


A.3 Prototype Vehicles

Ford C-MAX Energi and C-MAX Hybrid

The Ford C-MAX is considered to be a crossover vehicle. Both the C-MAX Energi and Hybrid use advanced Li-ion battery systems located in the rear of the car. The C-MAX Energi is the company's first-ever plug-in hybrid production electric vehicle that comes to market beginning in 2012, and the C-MAX Hybrid is a next-generation hybrid.

Component Location – The Li-ion battery appears to be mounted under the rear seats or in the trunk.



<http://prsync.com/batteryfast/-by-batteryfastcouk-lithium-battery-news-global-development-for-lithium-battery-manufacturing-114380/>
<http://lithiuminvestingnews.com/2585/global-development-for-lithium-battery-manufacturing/#>

Jeep Wrangler EV

The Jeep Wrangler EV is a two-wheel-drive HEV with an internal-combustion engine acting as a generator to feed electricity to both the battery and the electric motor. Using a combination of the electric motor and gasoline engine will allow this vehicle to travel up to 400 miles on a 10-gallon tank of fuel.

Component Location – The battery pack appears to be in the front of the vehicle.



www.jpmmagazine.com/featuredvehicles/154_0901_jeepp_wrangler_ev/photo_05.html
www.automobilemag.com/green/news/0901_2010_jeepp_wrangler_unlimited_ev/index.html
www.greenfuelsforecast.com/ArticleDetails.php?articleID=699

Fisker Karma

The Fisker Karma is four-door sedan on the green track but maintaining the sport and performance of the vehicle. The Karma is powered by a 2.0-liter turbo four-cylinder gasoline engine and twin 150-kW electric motors with a Li-ion battery pack. This vehicle is anticipated to have a battery-only range of 50 miles and a 300-mile range extended capability

Component Location – The 315 cell Li-ion battery pack is located where the transmission/prop-shaft tunnel normally would; attached lengthwise similar to the Chevrolet Volt.

www.windingroad.com/articles/reviews/driven-2012-fisker-karma/
www.insideline.com/fisker/karma/2012/2012-fisker-karma-first-drive.html



Mercedes Benz S-400

This is the first Mercedes with a hybrid drive using Li-ion battery packs. Since the drive of this vehicle uses a hybrid system it can maintain its high-power profile with a 3.5L V6 gas engine instead of the customary V8 or V12. This luxurious hybrid includes a hybrid gauge showing the flow of power between engine, battery, and regenerative braking.

Component Location – The battery pack is located at the right hand base of the windshield and weighs about 120 pounds.

<http://reviews.cnet.com/sc/33975778-2-440-SS01.jpg>
www.mbusa.com/mercedes/vehicles/explore/performance/class-S/model-S400HV



© 2010 CBS Interactive

Mercedes AMG E-Cell

This is also known as the “super car” with 526 horsepower and 649 pound feet of torque. This vehicle is said to have a hefty price tag, but the technology will most likely trickle down to their hybrids. The single charge battery range is 100 miles.

Component Location – “The lithium-polymer battery sits in front of the firewall, in the center tunnel and behind the seats to optimize weight distribution.”

www.wired.com/autopia/2010/06/mercedes-amg-sls-e-cell/#



Ronaele Mustang 600E

This muscle car starts as a high-performance Mustang with an internal combustion engine. This vehicle is manufactured by Ronaele Inc.; they purchase brand new Mustangs, remove the internal combustion engine, and replace the components with an electric engine. Ronaele Mustang comes in a couple different classes 300E and 600E. Lithium-ion or lithium iron phosphate battery packs replace the fuel tank powering this vehicle to up to 600 hp. The top speed of this vehicle is 130 mph with a battery range of 100-125 miles when driven at moderate pace.

Component Location – Not available.



www.greencar.com/articles/fast-times-mustang-300e-electric-musclecar.php

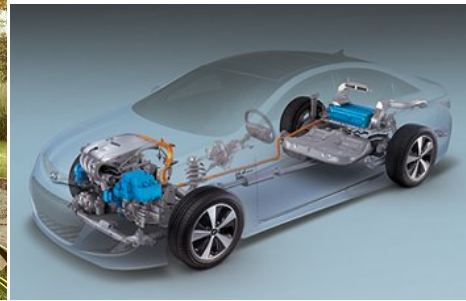
Hyundai Sonata

The Hyundai Sonata hybrid vehicle is Hyundai's first hybrid vehicle in the US market. This vehicle uses a polymer gel as the electrolyte in its battery; the next-generation Li-ion battery provides more power, less volume, and less weight. This vehicle is also equipped with Hyundai's Blue Drive technology made up of:

- An electric motor
- Regenerative braking system
- Integrated starter generator
- Theta II 2.4 liter engine
- 6-speed automatic transmission.

This system provides 206 net horsepower and delivers 35 to 45 mpg.

Component Location – The lithium polymer battery pack is located in the forward portion of the trunk, maximizing cargo space.



www.hyundaiusa.com/sonata-hybrid/



Volvo V70

The Volvo V70 is a hybrid vehicle with a diesel engine that engages whenever extra power or speed is needed or when the battery charge is low. Utilizing a combination of a 205 bhp diesel engine driving the front wheels, and a Li-ion battery and 70 bhp electric motor driving the rear, the vehicle is capable of getting 149 mpg. Also the vehicle can travel 30 miles in electric-only mode.

Component Location – It is unclear where the Li-ion battery is located, but Volvo is conducting research on integrating batteries into body panels.

www.timesonline.co.uk/tol/driving/new_car_reviews/article6858851.ece
www.plugincars.com/volvo-v70-plugin-hybrid/review

A.4 Production Vehicles



www.autoguide.com/auto-news/2010/03/geneva-2010-audi-a8-hybrid-debuts-with-2-0-tfsi-engine-lithium-ion-battery.html

Audi A8 Hybrid

Audi takes advantage of their own 2.0 TFSI engine, a four-cylinder combustion unit, combined with an electric motor and Li-ion battery pack. Although this vehicle is a hybrid, it produces a total of 245-hp and 354 ft-lbs of torque, allowing it to be quick and economical on fuel.

Component Location – Mounted in the rear section, this compact state-of-the-art Li-ion battery weighs less than other types but is substantially more powerful.

BYD e6

BYD Automotive designed an all-electric crossover vehicle, the BYD e6. In the city of Shenzhen they used 40 of these vehicles in a taxi fleet. This vehicle is not scheduled to be sold in the United States until 2012.

Component Location – Not available.

www.treehugger.com/files/2008/04/byd-electric-car-e6-crossover-mpv.php#
http://en.wikipedia.org/wiki/BYD_e6



Chevy Volt

The Chevrolet Volt was the world's first mass-produced plug-in hybrid electric vehicle. This vehicle was voted 2011 Best Engineered Vehicle by the Automotive Engineering International (AEI) magazine. The Volt uses a series hybrid technology allowing it to be plugged in and recharged. The electric motor is powered by a Li-ion battery and a 55kW generator that is turned by the use of gasoline in an internal combustion engine. The unique Li-ion battery enables the Volt to travel 40 miles without gas. The 240-volt Voltec home charging unit can charge the unit in about 4 hours. Also a significant amount of energy is returned to the battery via the Volt's regenerative braking system. LG Chem's exclusive reinforced separator provides improved safety.

Component Location – The Volt's Li-ion battery is constructed down the center tunnel of the car and out to either side under the rear seat area, to form a "T" shape.

www.popsoci.com/cars/article/2011-01/gm%E2%80%99s-new-battery-chemistry-it%E2%80%99s-already-chevy-volt

http://news.uchicago.edu/sites/newsmachine.uchicago.edu/files/imagecache/image_landingpage_zoom/images/image/20110107/rpvnqbcadm.10058.20110107.jpg

http://media.gm.com/content/dam/Media/microsites/product/volt/docs/battery_101.pdf





CODA Automotive

This all-electric vehicle can accommodate 5 adults and has a large trunk space. The CODA uses the Li-ion battery system with cutting edge technology for the battery management and thermal management systems. The battery range is 90 to 120 miles with a top speed of 80 mph.

Component Location – The 700 pound Li-ion battery cells are directly underneath the passenger compartment, low to the ground, which can enhance the vehicle's handling.

www.codaautomotive.com/all-electric-car/
<http://cdn-www.greencar.com/images/miles-coda-battery-electric-car-coming-2010.php/miles-coda-layout.jpg>

Ford Focus

Production for the Ford Focus Electric will begin in 2012 at the Michigan Assembly Plant. This vehicle is expected to travel 100 miles on battery alone. The Li-ion battery packs are being constructed by CPI (Compact Power Inc.). A cooled and heated liquid is used to regulate battery temperature and extend driving range.

Component Location – The Magna (Li-ion battery) will be located in the rear of the vehicle.

<http://reviews.carreview.com/blog/first-impressions-2012-ford-focus-ev/>
www.autoblog.com/2010/09/04/2012-ford-focus-ev-to-use-liquid-cooled-lithium-polymer-battery/



Li-Motors INIZIO RTX

The INIZIO RTX is manufactured by Li Motors Corporation, specializing in high speed Li-ion vehicles. This vehicle is the fastest of a family of three classes. The Li-ion battery pack propels this vehicle up to 170 mph with a range of 200 miles.

Component Location – Not available.

www.li-ionmotors.com/



Li-Motors WAVE SE

The WAVE SE is a two-passenger vehicle; the unusual shape makes the vehicle more aerodynamic, decreasing the drag. The Wave SE is the big brother to the Wave S; they are the same make and model but the Wave SE is upgraded with higher performance. This vehicle has a top speed of 90 mph. This vehicle won the Progressive Insurance Automotive X PRIZE.

Component Location – Not available.

www.li-ionmotors.com

Li-Motors LiV Flash

The Li-Motors LiV Flash vehicle is considered to be a plug-in-battery vehicle. This vehicle is equipped with a 3 Phase Brushless AC Motor powered by 550 lbs of Li-ion battery packs. When fully charged it has a range up to 120 miles.

Component Location – Not available.



www.li-ionmotors.com/

Li-Motors LiV Harmony

The LiV Harmony is a five-passenger battery electric vehicle with a top speed of 80 mph and a battery-only range of 120 miles. This vehicle uses touch screen technology to display available miles, power consumption, cell charge levels, battery temperature, drive time, and average speed.

Component Location – Not available.

www.li-ionmotors.com/



Li-Motors LiV Wise

The 2-door LiV Wise is manufactured by Li-Motors and promises a range of 120 miles per full charge. This vehicle can also reach speeds of 80 mph.

Component Location – Not available.

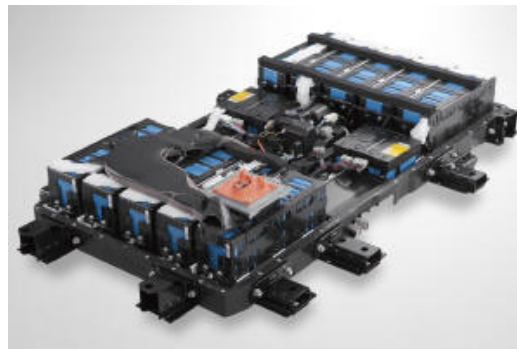
www.li-ionmotors.com/



Mitsubishi iMiEV

The Mitsubishi innovative electric vehicle uses lithium manganese oxide based battery chemistry and has a battery-only range of 100 miles. The iMiEV was used for fleets in Japan in 2009 and made available in the U.K. in 2011.

Component Location – The battery packs are located under the base of the floor in the same location as in the Peugeot iOn.

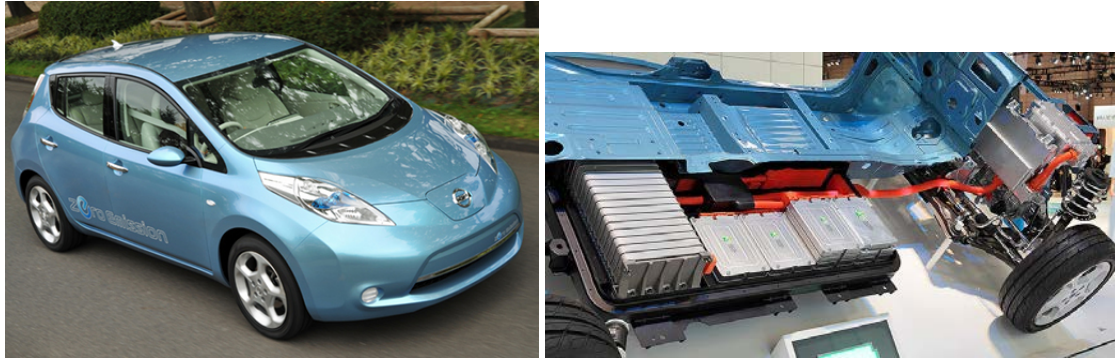


www.google.com/imgres?imgurl=www.autopressnews.com/2009/06/Mitsubishi/i-MiEV_battery_pack.jpg&imgrefurl=www.autopressnews.com/2009/06/Mitsubishi/EV_i-MiEV.shtml&usq=_qOShWHvWJapKQ05r2LMx9eV2F-I=&h=200&w=300&sz=12&hl=en&start=5&zoom=1&itbs=1&tbnid=dgq0w4DaZqwlVtM:&tbnh=77&tbnw=116&prev=/images%3Fq%3DMitsubishi%2509iMiEV%2Bbattery%2Blocation%26hl%3Den%26sa%3DX%26rls%3Dcom.microsoft:*%26rlz%3D117RNSN_en%26tbs%3Disch:1%26prmd%3Divns&ei=KhKWTFDFGe6E0QGx2bT5Cw
www.insideline.com/mitsubishi/i-miev/first-drive-2010-mitsubishi-i-miev-plug-in-electric.html

Nissan Leaf

The Nissan Leaf is the world's first volume production electric car. This midsize hatchback is capable of getting 100 miles on a single charge and is in direct competition to the Chevy Volt, Toyota Prius, and Ford Focus Electric.

Component Location – The Li-ion battery pack comprises 48 modules and 192 thin laminated cells. The battery pack is located under the seats and floor.



www.examiner.com/green-transportation-in-national/turning-over-the-nissan-leaf-to-look-inside
<http://green.autoblog.com/2010/05/27/details-on-nissan-leaf-battery-pack-including-how-recharging-sp/>

Peugeot iOn

The Peugeot iOn has been in production since 2009 in Europe. The Peugeot iOn is a rear-wheel drive vehicle in which the electric motor and single-ratio reduction gearbox are installed in front of the rear suspension. The battery pack allows this vehicle to travel 93 miles on battery power.

Component Location – The battery pack is housed on the floorboard.



www.netcarshow.com/peugeot/2009-ion_concept/
www.google.com/imgres?imgurl=http://autobuzzi.com/images//2011-Peugeot-iOn-Battery-608x429.jpg&imgrefurl=http://autobuzzi.com/2011-peugeot-ion-electric-full-size-cars-with-cooled-battery/&h=429&w=608&sz=31&tbnid=4j77NJ8XwQ1GEM:&tbnh=96&tbnw=136&prev=/images%3Fq%3D2009%2BPeugeot%2BiOn%2BBattery%2Bpictures&zoom=1&q=2009+Peugeot+iOn+Battery+pictures&hl=en&usq=x8CYR3jhRb15xcDJY8Jy_ITJqWo=&sa=X&ei=7wuWTbHkF9CP0QGr04D1Cw&ved=0CBwQ9QEwAQ





Tata Nano

This battery-electric vehicle uses a super polymer Li-ion battery to propel it to 80 mph. It also has a battery-only range of 100 miles.

Component Location – Not available.

<http://inhabitat.com/all-electric-tata-nano-revealed-in-geneva/>

Tesla Roadster

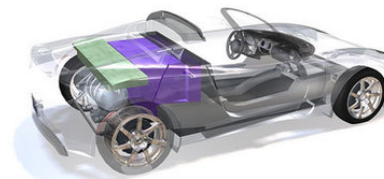
The Tesla Roadster was developed by Tesla Motors and made available in 2008. A 3-phase alternating current induction motor powers the Tesla Roadster. The unique 6,831 Li-ion cells make up the battery pack, allowing the Tesla to travel 245 miles on a full charge.

Safety features for the Tesla Roadster battery system have been integrated at the cell and pack level, some of which include:

- Internal positive temperature coefficient current limiting device
- Current interrupt device
- Mechanical, thermal, and chemical factors
- Cell connection
- Smoke, humidity, and moisture sensors.

The Tesla Roadster has passed all existing Federal Motor Vehicle Safety Standards (FMVSS), including crashing complete cars with working batteries.

Component Location – The 3-phase, 4-pole electric motor is located in the trunk of the vehicle and the Li-ion battery pack appears to be in the rear of the vehicle directly behind the driver and passenger seats.



<http://blogs.edmunds.com/greencaradvisor/2009/02/tesla-battery-pack-replacement-would-be-36000-today-musk-says.html>
http://webarchive.teslamotors.com/display_data/TeslaRoadsterBatterySystem.pdf

Tesla Model S

The Tesla Model S was developed by Tesla Motors and made available in 2012. It is a rear wheel drive electric vehicle. The powertrain includes the battery, motor, drive inverter, and gear box. It has a microprocessor controlled, Li-ion battery powering a three phase, four pole AC induction motor with copper rotor. The Model S has variable frequency drive and regenerative braking system. An estimated 7,000 to 8,000 Li-ion cells make up the battery pack, available in 40, 60, and 85 kWh sizes, the largest of which allows the Model S to travel up to 300 miles on a full charge.

The Tesla Model S battery system is liquid-cooled, to maintain consistent temperatures and to prevent cells from overheating. In the event of a crash, the battery structure protects cells from impact and automatically disconnects the power supply. The battery protects its contents and augments the overall strength of the passenger cabin.

Model S is engineered with the intent to achieve 2013 five-star NHTSA safety ratings. Final safety data are not yet available.

Component Location – The electric motor is located in the rear axle area and the Li-ion battery pack appears to be in a wide, shallow case beneath the entire driver and passenger areas.



www.teslamotors.com/models

Toyota Prius

The Prius PHV is based on the third-generation Prius and is anticipated to get 50 mpg using Li-ion battery packs. The Prius PHV is capable of accelerating to 60 mph on electric-only power.

Component Location – The battery pack is located in the trunk directly behind the back seat of the vehicle.

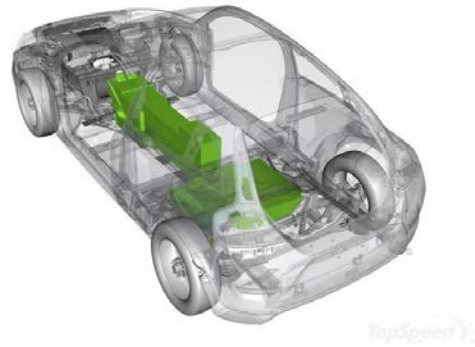
www.luqman-technologies.com/seo-agency/wp-content/uploads/2011/01/Toyota.bmp
www.hybridcars.com/files/prius-battery-pack-400.jpg



2010 Volvo C30

A number of prototype versions of C30 BEV were designed and internally tested in 2009. Starting in 2011 the C30 BEV prototype will be tested by at least 50 select users. Running entirely on electricity, the Volvo C30 tops out at 81 mph with a battery-only range of 93 miles.

Component Location – The Li-ion battery pack is located in the prop shaft tunnel and in the place where the fuel tank normally is located.



www.motortrend.com/auto_shows/detroit/2010/0912_volvo_c30_bev/index.html
www.topspeed.com/cars/volvo/2010-volvo-c30-bev-ar79267.html

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**National Highway
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